THE SORPTION OF THORIUM, PROTACTINIUM, AND PLUTONIUM ONTO SILICA PARTICLES IN THE PRESENCE OF A COLLOIDAL THIRD PHASE

A Dissertation

by

KIMBERLY ANN ROBERTS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2008

Major Subject: Oceanography

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Chair of Committee,	Peter H. Santschi
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ABSTRACT

The Sorption of Thorium, Protactinium, and Plutonium onto Silica Particles in the Presence of a Colloidal Third Phase. (May 2008)

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The fate of actinides in the environment is of interest for a several reasons. In oceanic surface waters actinides such as thorium and protactinium, and in particular their ratio, are used as tracers of processes such as boundary scavenging and paleocirculation. Thorium is also used to estimate residence times and particle and colloid fluxes from the euphotic zone, which is useful in global carbon budgets used to assess effects of global warming. Terrestrially, contaminated areas in need of remediation, such as former nuclear weapons production facilities, remain as repositories for no longer needed actinide stockpiles or waste by-products such as plutonium. All three of these actinides: thorium, protactinium, and plutonium are known to be particle-reactive but the extent to which they sorb to immobile particles and mobile colloids can vary with environmental conditions. Understanding controls on adsorption is important in understanding uses and any limitations of these radioactive tracers caused by colloids.

Often laboratory studies to understand actinide behavior are conducted at concentrations (micro- to millimolar), which are orders of magnitude higher

than they are found in the environment (femto- to picomolar). Colloids, a size class of particles operationally defined as 1 nm to 1 μm in size, are ubiquitous in aquatic systems. The effect colloids have on actinide particle association, i.e. competitive or enhancing, can have a profound influence on the ultimate behavior of the actinide.

The overall aim of this study is to assess sorption of thorium, protactinium and plutonium onto silica particles as a proxy for inorganic particles found in surface or ocean waters. In addition to the binary system of actinide/silica, the ternary system actinide/ organic colloid/ silica were also carried out to determine the affect of the organic colloid has on particle association. In particular, extracellular polymeric substances (EPS) extracted from laboratory grown bacteria and phytoplankton cultures were utilized as they too are ubiquitous in aquatic systems and have shown to strongly complex actinide ions, with EPS involved in oceanic scavenging of Th, as well as immobilization/mobilization of Pu in contaminated areas on land.

To my mother,

who has taught me the true meaning of strength and perseverance

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I would like to thank all of my colleagues at the Laboratory for Oceanographic and Environmental Research (LOER) at Texas A&M University at Galveston, especially Dr. Chin-Chang Hung and Ms. Chen Xu for production and characterization of the EPS used for this study, and Mike Andres for invaluable help near the end. I would like to thank the crew of the RV Seward Johnson, Maureen Conte for BATS samples and accompanying data and David Karl for HOT samples. A very special thanks goes out to Mary Howley and Sherry Parker for all of their help in making many of the day to day aspects of research (and reimbursement) go smoothly and to Sandy Drews for all of her running for signatures. Thanks to Dr. Tammy Holliday, Peggy Rutowski and everyone in the Office of Research and Graduate Studies at TAMUG.

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1. INTRODUCTION

1.1 Introduction

The fate of actinides in the environment is controlled by a variety of processes. Figure 1.1 from Runde depicts the complex behavior of actinides in the environment, including complexation, redox, dissolution/precipitation, sorption, bioavailability, and transport. Though bioavailability and dissolution/precipitation reactions can affect actinides, this study will not address these processes. Instead the focus here will be primarily on sorption, complexation and redox of multi-valent actinides. Redox reactions and the resulting oxidation state of mulit-valent actinides such as plutonium will control its sorption and complexation behavior, and thus, its ultimate fate. Therefore, all three of these processes determine the mobilization or immobilization of a given actinide.

The speciation and transport of stable and radioactive metals, which are present in aquatic systems at very low concentrations, is controlled by a) thermodynamics, e.g., solubility of least soluble phase, solution and surface complexation, and b) sorptive uptake and transport by organic or inorganic pseudocolloids, i.e., carrier colloids of a different composition than the metal ion in question. Since actinides (with the exception of soluble U(VI)) are present in aquatic systems at femto- to pico-molar concentrations, and the concentration of organic and inorganic colloids is of the order of micromolar in surface waters (Santschi et al., 1995, 2002) to nanomolar in drinking water (Bundschuh et al.,

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This dissertation follows the style of Applied Geochemistry.

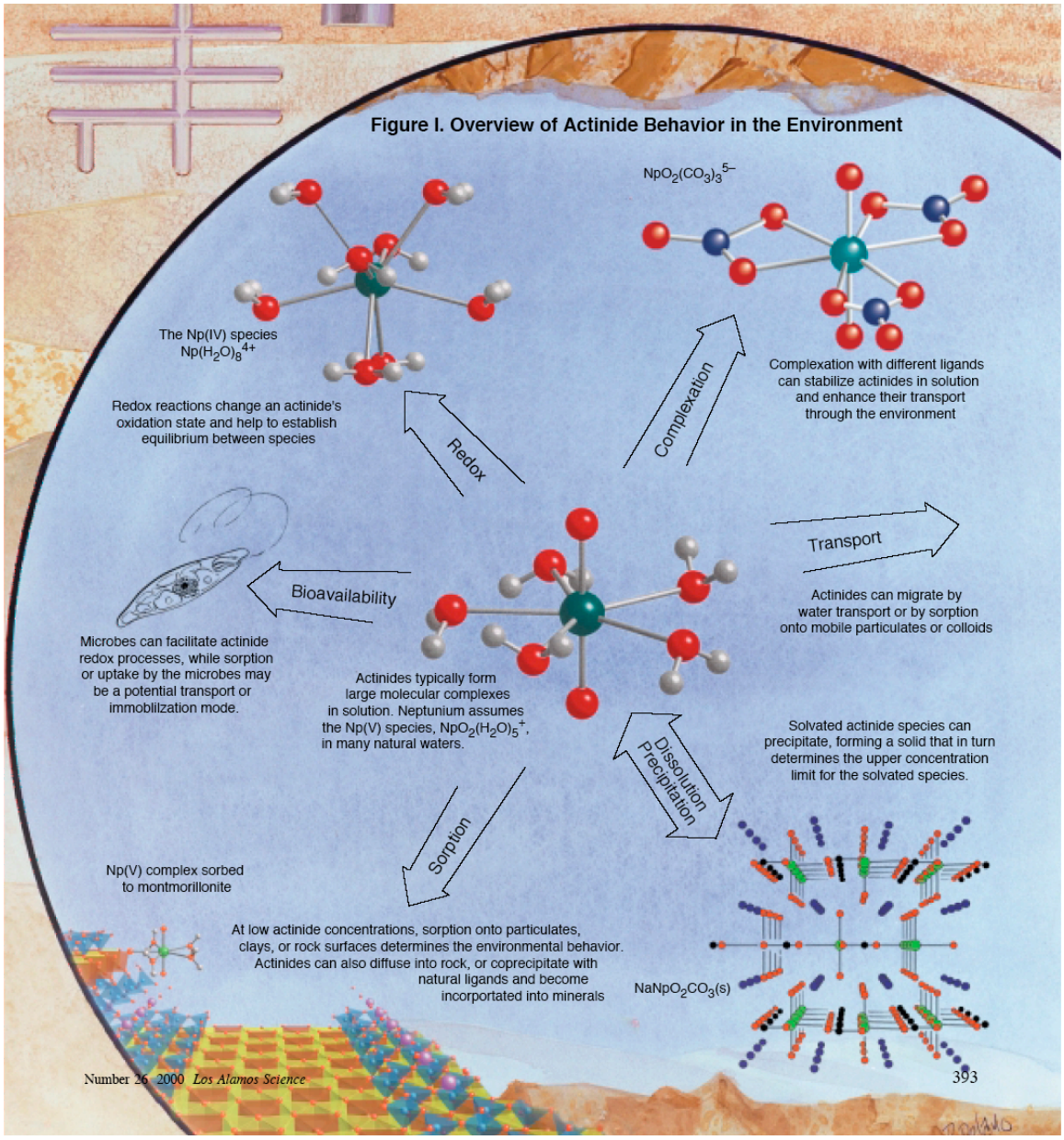

Figure 1.1. Overview of actinide behavior in the environment from Runde, W., 2000.

2001), hydrolytic actinide species are most likely not able to form their own phase but tend to associate with a carrier phase, i.e., a pseudocolloid. There is considerable evidence that speciation and transport of 4-valent actinides such as Pu(IV) or Th(IV) in aquatic environments is controlled by pseudocolloids, e.g., Si-Al-hydroxides (Doucet et al., 2001; Panak et al., 2003; Kim et al., 2003), polysaccharide-rich exopolymeric substances (Quigley et al., 2002), or Fe-organic colloids (Santschi et al., 2002). According to the analysis of Dequeldre et al. (2000), the observed stability of pseudocolloids in groundwaters depends on dissolved organic carbon concentration and pH. There are, however, only a few studies where the carrier phase or molecular assemblies of actinides have been identified or characterized.

Environmental studies have demonstrated that some metals and radionuclides, mainly A-type hydrolytic III- and IV-valent metal ions, have a strong affinity for particles and colloids or nanoparticles (Honeyman, 1991; Honeyman and Santschi, 1989, 1991; Quigley et al. 2001). This has implications on environmental issues in that the speciation of metals can affect the transport, toxicity, or bioavailabilty of potential toxins (Gaillard, 2001). Traditionally, metal ions in natural waters have been operationally separated into particulate and dissolved fractions using a 0.45μm filter. More recently, studies have further fractionated the dissolved fraction using ultrafilters. Santschi et al. (2002) analyzed the size fractionation of ^{239,240}Pu and ^{241}Am in surface and groundwaters and found that up to 80% of the operationally defined

"dissolved" activity was in the fraction that was passing a 0.45 μm filter but was retained by a 3 kDa ultrafilter, i.e., was in the "colloidal fraction".

A few laboratory studies have addressed the sorption behavior of Th and Pa tracers to natural surfaces under ambient conditions (e.g., Guo et al., 2002; Geibert and Usbeck, 2004), but have failed to adequately take into account the issue of ambient colloids, clean surfaces, or the production of particulate phases of Th and Pa tracers from ambient colloids without any particle surfaces present. For example, Geibert and Usbeck (2004) reported particulate fractions of these tracers in solution without particle surfaces that were considerably higher than with some of these particle surfaces present, but then went on to ignore such artifactual results.

1.1.1 Thorium

Thorium is found in the natural radioactive decay series as either a daughter of Uranium (e.g., ^{230}Th, ^{234}Th), Radium (e.g., ^{228}Th), or as the parent of a decay series (^{232}Th) Thorium has only one oxidation state, IV. As Th(IV), it is known to be strongly particle-reactive. Chemical studies on the behavior of thorium in natural waters show that thorium is either complexed with organic ligands (e.g., Choppin, 1983, 1989) or present as a $Th(OH)_4^o$ (Langmuir and Herman, 1980; Kim et al, 2003; Panak et al., 2003, Fanghänel and Neck, 2002; Walther, 2003) and $Th(OH)_3CO_3^-$ (Bruno, 1990; Östhols et al., 1997; Murphy et al., 1999) complex. The solution and surface chemistry of Th(IV) has been summarized by Murphy et al. (1999) and Reiller et al. (2002, 2003). $Th(OH)_4$ and ThO_2 solubility is about 10^{-9} M (± one order of magnitude), regardless of

crystallinity (Neck et al., 2003). However, natural concentrations are orders of magnitude lower, e.g., picomolar for ^{232}Th in the ocean (Huh et al., 1989). Therefore, environmental concentrations of Th(IV) are either near or below the solubility limit. Th complexation with various low molecular organic and inorganic ligands is summarized in Table 1.1.

Table 1.1
List of pKa values and stability constants for Thorium/Ligand Complexes $Th^{4+} + L^{n-} = ThL^{(4-n)+}$

Ligand	Log b_1	Log b_2	Ref.	pK_{a1} (pK_{a2}) of acid
OH^-	10.2	20.0	1	14
CO_3^{2-}	11.0		1	6.3 (10.25)
F^-	7.3	3.2	1	3.2
SO_4^{2-}	3.67		1	-9 (2.0)
Cl^-	0.36		1	-7
HPO_4^{2-}	10.8	22.8	1	2.15 (7.2)
NO_3^-	0.94	2.0	1	-1.4
Acetic acid	3.1		2	4.72
Oxalic acid	9.3	18.5	1	1.2 (4.2)
Malonic acid	7.58		2	2.85 (5.07)
Succinic acid	6.44		2	4.2
Humic acids	10-11	15-17	3	4.5
Citric $acid^{3-}$	13.0		1,2	3.06
$EDTA^{4-}$	23.2		2	1.70 (2.6)
$HEDTA^{3-}$	17.0		2	2.51 (3.6)
IDA	9.69		2	2.6 (9.2)
NTA^{2-}	15.2		2	1.9 (2.5)
$CDTA^{4-}$	25.6		2	2.4 (3.5)
$EGTA^{4-}$	20.5		2	2.0 (2.66)
DTPA	27.1		2,4	2.0 (2.6)
Benzo-1,3-dioxole-2,2-diphosphonic acid	16.4		2	1.9 (6.35)
Catechol, 1,2-dihydroxy benzene	5.5		4	9.3 (13.3)

1. Langmuir and Herman (1980); Choppin (1989)
2. Martell and Smith (1990); Smith and Martell (1989)
3. Nash and Choppin (1980)
4. Hirose and Tanoue (2001)

1.1.2 Protactinium

Like thorium, protactinium is also a highly particle reactive element. However, the chemistry of protactinium is more complex in large part because protactinium has three possible oxidation states (IV, V, VI) in natural waters (Alhassanieh et al, 1999). The predominant form is likely Pa(V) in oceanic systems (Choppin, 1983), which, as a PaO_2^+ ion, is quite soluble, similarly to the Pu(V) ion, and sorbs to particle surfaces to a much lower extent than the four-valent oxidation state ion, Pa(IV). It is likely that Pa(V) is first reduced to Pa(IV) before adsorption and removal from natural waters can take place, as has been seen for Np(V), which is reduced in the presence of natural organic matter such as humics (Zeh et al., 1999). Organic ligands such as extracellular polymeric substances (EPS) produced by bacteria and phytoplankton are another possible source of reductants and this will therefore be one of the focal areas of this study. Very little is known not just about the complexation, but also about the redox behavior in aquatic systems. What is known is the redox potential for Pa(V) to Pa(IV) reduction is -0.05V, as shown below.

$Pa(V)O_2^+ + 2\ H_2O + e^- = Pa(IV)(OH)_4$; E_h^o=-0.05V

(Greenwood, N.N., and Earnshaw, A. 1998.)

Possible biologically mediated redox reactions include aldehydes, hydrogen sulfide, ferridoxin, and semiquinones, as shown below for pH of 7 (Stumm and Morgan, 1996).

$FeOOH(s) + HCO_3^-(10^{-3}\ M) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$; $E_h^o(w) = -0.05$ V

$1/6\ SO_4^{2-} + 9/8\ H^+ + e- = 1/8\ HS^- + 1/2\ H_2O$; $E_h^o(w) = -0.22$ V

$1/2\ HCOO^- + 3/2H^+ + e^- = 1/2\ CH_2O + 1/2\ H_2O$; $E_h^o(w) = -0.45$ V

¼ $CO_2(g) + H^+ + e^- = 1/14\ C_6H_{12}O_6$ (glucose) + ½ H2O $E_h^o(w) = -0.4$ V

oxidized ferridoxin + e- = reduced ferridoxin $E_h^o(w) = -0.4$ V

In addition, microbially produced flavodoxins have a $E_h^o(w)$ of – 0.3 to -0.4 V (Hoover et al., 1999) and flavin mononuleotides have a $E_h^o(w)$ of – 0.2 V, which is lower at higher pH (Mayhew, 1999). From these redox potentials at pH of 7, one might expect that a number of microbially produced molecules as well as simple polysaccharides would be able to abiotically reduce Pa(V) to Pa(IV).

1.1.3 Plutonium

Pu is another actinide that has a complex chemistry due to the occurrence of multiple oxidation states. For example, Pu(V) is the main oxidation state in aquatic environments with low natural organic matter concentrations, e.g., glacier ice, open ocean waters, or some ground waters (Choppin and Wong, 1998; Choppin, 2003; Choppin and Morgenstern, 2001). As Pu(V), it is quite soluble and not very particle-reactive. In aquatic environments with higher DOM concentrations such as surface waters, Pu(IV) is the main oxidation state (Choppin and Morgenstern, 2001; Choppin and Wong, 1998). The redox potential for the Pu(IV)/Pu(V) couple is +1.17V at pH=0, +0.70±0.12 at pH=8, and +0.52±0.24V at pH=14 (Allard et al., 1980; Choppin, 1983, 2007; Choppin et al., 1997). The main solution species for Pu(IV) is $Pu(OH)_4^o$, and for Pu(V), it is PuO_2^+ and PuO_2^+ and $PuO_2CO_3^-$ (Choppin et al., 1997). The solubility of PuO_2 or $Pu(OH)_4$(am) is of the order of 10^{-8} M (Runde et al., 2002; Fanghänel and Neck, 2002). However, Pu is generally found at much lower concentrations in the

aquatic environment, e.g., at femtomolar levels, mainly due to anthropogenic activities such as bomb fallout. However, there are places where Pu contamination is more prevalent in surface environments, but it is rarely seen above pM concentration levels. As particle-reactive Pu(IV), it can be expected to be bound to organic molecules, which can lead to either trapping or mobilization, depending on environmental conditions (e.g., DOC concentration, ionic strength and pH). In accordance with this, a recent study (Santschi et al., 2002) indicates that the colloidal organic matter could be a significant mechanism for transporting Pu in watersheds. A general view of speciation of plutonium in natural waters (from Runde, 2000) is found in Figure 1.2.

1.1.4 Actinide adsorption on particles and colloids

In Oceanography, certain actinides have been used as tracers of particle-related removal processes. For example, short-lived ^{234}Th has been used to determine fluxes of organic matter from the upper water column, and longer-lived ^{231}Pa and ^{230}Th, as well as their ratio, have been used in ocean circulation, boundary scavenging and paleoproductivity studies. Evidence from the upper water column studies has suggested that Th may preferentially scavenge to organic matter. Thus, POC/^{234}Th ratios, combined with calculated ^{234}Th fluxes, have been on of the main ways to determine export production (e.g., Buesseler et al., 1992; Bacon et al., 1996, Moran et al., 2003; Santschi et al., 1999, 2003). Because the ratios vary as a function of depth and size (Walter et al., 2001), other factors such as the type of organic matter might be responsible for controlling the variability. The fractionation of Pa from Th in the ocean might be controlled

by the initial reduction of the more soluble Pa(V) to the more particle-reactive Pa(IV). There is currently also a controversy as to the type of inorganic sorbent

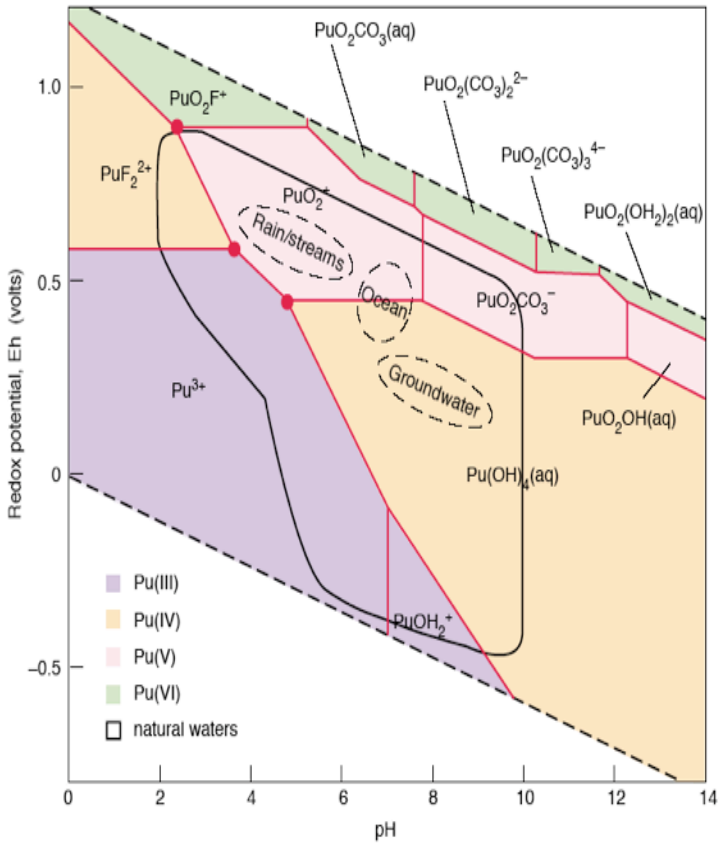

Figure 1.2. Pourbaix diagram for plutonium from Runde, W., 2000.

that is responsible for scavenging of Th and Pa isotopes from ocean water. Some researchers attribute the changing Pa/Th ratios to enhanced scavenging of Pa onto biogenic opal (Luo and Ku, 1999), while others (Chase et al., 2002) believe that it is clay minerals that preferentially scavenge Th over Pa. However, based

on the thermodynamic information at hand, clays, silica, nor any other mineral phase can fully account for the observed fractions of these isotopes on particles that are observed in ocean waters. Table 1.2 is a compilation of reported sorption data of Th or Pa on mineral or organic phases, which demonstrates that the only possible compound that has been identified to date to account for the observed particulate fraction is a polysaccharide-enriched phase common in particles and colloids. This further demonstrates the need for a better understanding of the chemical nature of the colloidal carrier phases of actinides in the ocean as well as fresh waters.

Laboratory studies have been conducted to study adsorption of actinides on particles as well as colloids. The past and present emphasis of such studies focused on inorganic particles (Morse & Choppin, 1986; Hunter et al. 1988; Geibert & Usbeck, 2004). As the importance of natural organic matter became apparent, humic substances were included (Nash & Choppin, 1980; Choppin & Nash, 1981; Reiller et al., 2002). To date very limited research has been conducted with other natural organic compounds, especially of higher molecular weight, such as biopolymers from the ocean (Murphy et al., 1999; Quigley et al., 2001; Hirose & Tanoue, 2001). Important but so far little explored metal-complexing biopolymers include the hydrophilic acid polysaccharide-containing exopolymeric substances (EPS), which can also contain more hydrophobic proteins or lipids (as glycoproteins or lipopolysaccharides), thus making them amphiphilic (or surfactant-like). EPS in the ocean are responsible

for the formation of marine and lake snow, gels and biofilms (e.g., Verdugo et al., 2004).

Table 1.2
Predicted fraction on particles for ^{234}Th(IV) onto mineral phases in the open ocean, based on observed lab-based particle-water partition coefficients, Kd {L/kg}, and upper limits of observed field-based particulate concentrations, Cp {kg/L}, to be compared to observed fp that range from 0.1 to 0.5.

Mineral or organic Phase	**Log Kd (L/kg)**	**Reference***	**-Log Cp (kg/L)**	**Fp (predicted)**
SiO_2	3-5	Our data	8	$<10^{-3}$
$CaCO_3$	4-5	1,2	8	$<10^{-3}$
Al_2O_3/Clays	5.6	3	9	$<10^{-3}$
FeOOH	5.1-5.8	2,4	9	$<10^{-3}$
MnO_2	4.4	2,5	9	$<10^{-4}$
EPS@100% PS	8	6	8	0.5

***References:**

1. Edwards et al., 1987; Cochran, 1992; 2. Guo et al., 2002;
3. Niven and Moore, 1993; 4. Quigley et al., 1996.; 5. Hunter et al., 1988;
5. Quigley et al., 2002.

1.1.5 Colloidal actinide remobilization

A recent study of resuspension of Pu-contaminated soil from Rocky Flats Environmental Technology Site showed enhanced remobilization of Pu in the presence of humic and fulvic acids (Santschi et al., 2002). Through the use of SDS-PAGE and electrophoretic focusing (IEF), this study also demonstrated that the Pu is associated with an organic macromolecule of 10 kDa molecular weight and isoelectric point (pH_{IEP}) of about 3, which would make it negatively charged at neutral pH. Pu in the sample also closely followed Th(IV) and Pu(IV) that were added to the samples, thus strongly suggesting a 4-valent oxidation state for the ambient Pu. Pu in IEF was also at the same pH_{IEP} as polysaccharides

(radiolabeled at their OH groups), and some of the iron, but not Si or Al, strongly suggesting organic iron colloids as the carrier molecule. Last but not least, humic acids, as well as other organic acids (but not acid polysaccharides, APS), added to the soil suspension, had a strong effect in remobilizing colloidal Pu from the soil. Thus, while humics and fulvics from soils have the capacity to remobilize Pu (Santschi et al., 2002), other compounds such as APS or EPS, produced by bacteria may offer a means for immobilization.

1.2 Objective

The overall objective of this study is to gain a better understanding of the role of organic colloids (EPS) in the processes that can lead to actinide mobilization or immobilization on particle surfaces in freshwater and marine systems.

1.3 Hypotheses

1) Interactions between actinides and functional groups on organic colloids control speciation and transport in aquatic systems.

2) Reducing moieties of organic colloids have the capacity to reduce 5-valent (Pu(V) and Pa(V)) to 4-valent (Pu(IV) and Pa(IV)).

3) Hydrophobic moieties (e.g., proteins) on EPS can render the carrier macromolecule more surface-active (i.e., more surfactant-like; Ron and Rosenberg, 2001), and thus, lead to greater particle associations.

1.4 Experimental Approach

A ternary adsorption system, consisting of an inorganic particle, an organic colloid and the actinides, thorium, protactinium and plutonium will be studied to address the hypotheses. This study will consist of 4 major components: 1) test of experimental conditions, 2) testing of the reducing capabilities of organic colloids, i.e., exopolymeric substances (EPS) and humic acids, on Pu(V), 3) compare field measurements with archived samples and literature values, and 4) conduct a systematic study of sorption as a function of ionic strength and pH to gain insight on the type of interaction that is occurring, i.e., inner-sphere or outer-sphere complex from surface sorption as a function of I, and binding strength from surface sorption as a function of pH.

Table 1.3 Chemical composition of EPS from microbial and phytoplankton species. All concentrations are normalized to organic carbon (%OC) (*Sagittula stellata*, SS103106II), and *Pseudomonas Fluorescens* Biovar II, PFB011807I): Chen Xu, personal communication; *Pseudomonas fluorescens* Biovar II -2, *Synecococcus*, *Emiliani huxleyi*, *Skeletonema costatum*: Chin-Chang Hung, personal communication).

Species	OC (%)	TCHO (%)	Protein (%)	URA (%)	MW (kDa)[a]
Soil Bacteria					
*Pseudomonas fluorescens*Biovar II (011807I)	30	37	6	5.9±1.1	20.7±0.1
Pseudomonas fluorescens Biovar II -2	25	31	3	14	8 (125)
Estuarine Bacteria					
Sagittula stellata (103106II)	27	42	5.5	1.3±0.3	29
Marine Phytoplankton					
Synecococcus	22	13	3	1	8 (<8)
Emiliani huxleyi	6	58	2	7	<8 (8)
Skeletonema costatum	17	36	2	10	75 (<8)

[a]) Value in bracket indicates minor component.

1.4.1 Experimental conditions

Time will first be spent addressing the effect of different experimental conditions on resulting particle water partitioning coefficients (log Kd), e.g., clean conditions, particle-water separation and tracer neutralization approaches. Information regarding composition of EPS used in this study is available in Table 1.3 (Chen Xu and Chin-Chang Hung, personal communication).

1.4.2 Experiments testing the reduction of and Pu(V) using organic reductants

Experiments with commercially available organic molecules, such as glucose, formaldehyde, and humic acid, as well as model APS and EPS, will be carried out to determine if Pu(V) are reduced to four-valent state. Pu(V) will be made following the procedure of Saito and Choppin (1983). Determinations of whether or not a change in oxidation state has occurred will be carried out indirectly by comparing colloidal association and binding strength results with those of Pu(IV).

1.4.3 Comparison of newly acquired sediment trap material to archived material and particle water partitioning coefficients in the literature

Sorption experiments will be conducted while at sea on newly collected sediment trap material using Th, Pa, and Pu. Particle-water partioning coefficients (log Kd) values will be calculated and relationships to chemical composition of the sed trap material will be assessed. Additionally, log Kd values will be compared with archived sed trap material from times series

stations such as BATS (Bermuda Atlantic time series) and HOT (Hawaii Oceanic Time series).

1.4.4 A systematic study of sorption of Th, Pa and Pu with varying ionic strengths and pH

Finally, a more classical approach will be taken as these actinides, Th, Pa and Pu will be systematically studied as a function of ionic strength and pH. The pH will be determined using a series of non-interactive "better buffers" developed from the Good buffer series (Good & Izawa, 1972, Yu et al., 1997). Results will be compared, when available, to experimental data from the literature, or simple model predictions.

2. THE EFFECTS OF EXPERIMENTAL CONDITIONS ON THE DETERMINATION OF PARTICLE-WATER PARTITIONING OF PARTICLE REACTIVE ACTINIDES AT NEAR-AMBIENT ENVIRONMENTAL CONDITIONS

2.1 Overview

In order to probe the ionic or colloidal state of Th(IV) and Pu(IV) tracers at near-environmental, fM, concentrations and neutral pH, special attention has to be paid to their partitioning into different colloidal fractions with different surface reactivities that can be introduced inadvertently rather than purposely. For the purpose of probing the effects of colloids introduced or eliminated by different experimental conditions, a series of laboratory-scale studies were conducted to study how varying conditions would affect values of the traditional particle-water partition coefficient, Kd, to silica particles, as proxies of mineral particles. Results reveal the critical importance of procedures to separate particles from water and the maintenance (instead of initiation) of neutral conditions during these experiments. The results of these experiments are relevant not only for experimentalists, but for modelers as well. Any model that attempts to predict that sorption or transport of Th(IV) or Pu(IV) at fM to pM concentrations will need to take into account the presence of colloidal forms of these tracers in solution and on surfaces.

2.2 Introduction

There are several challenges when studying sorption reactions of particle-reactive actinides (Th and Pu) onto natural (inorganic and organic) particles in aquatic systems, which often contain organic or inorganic colloidal carrier phases. First, actinide ions occur at femtomolar concentrations in the environment, while surface and solution complexes occur at concentrations of at least micromolar, yet laboratory studies are often conducted at actinide concentrations that are close to those of the most abundant and weakest surface and solution ligands (Hunter et al., 1988, Reiller, et al., 2002, Geibert and Usbeck, 2004). Second, the tracers themselves come in an acidic solution, while the pH of natural aqueous solutions need to be close to neutral (pH~8), a condition that requires tracer pre-neutralization, with the danger of creating "pseudo-colloidal" metal hydroxy species upon neutralization, leading to the rapid and irreversible formation of colloidal actinides in the small volume of high pH before it is thoroughly mixed in. Such colloids could be produced from polyhydroxy polymers of iron or aluminum impurities from leachates of reagents stored in glass bottles. As a matter of fact, Al-silicate colloids have been identified and quantified even in drinking and distilled water at higher than fM surface site (Bundschuh et al. 2001). Kim et al., 2003 and Panak et al., 2003 demonstrated the formation of aluminosilicate colloids, and showed that these colloids strongly interact with actinides.

For example, in surface and subsurface waters, elemental ratios of dissolved or particulate Pu to its carrier-phases OC or Fe are never higher than

$1{:}10^{-6}$, not even in contaminated areas, but more often closer to $1{:}10^{-9}$, given typical average concentrations for R-COO- (organic acid), Fe and Pu near 10^{-6}, 10^{-7}, and 10^{-15} M, respectively. At these low Pu concentrations, any complexing and/or colloidal impurities in the experimental system can influence the results in uncontrollable ways, whereas at mM and μM concentrations of Pu that are often used, this would not be the case. However, at such elevated Pu concentrations, only the weakest binding sites would be studied, which under most circumstances have little relevance for our understanding of the natural environment.

Colloidal impurities are ubiquitous in aqueous solutions, and thus, it is likely that NaOH pre-neutralization of Th and Pu tracers can have been the cause of higher particle-water partition coefficients in control experiments (without any particles) than in experimental systems with particles, results that have been reported by Geibert and Usbeck (2004).

Furthermore, reagents are often already wrought with colloidal impurities, which can interfere with the colloid under study. Such colloids can interfere, for example in studies of how an organic colloidal phase affects actinide sorption on to inorganic mineral phases. In order to address such a question, one needs to be able to experimentally isolate the sorption process of the radioactive tracers onto a specific colloidal and/or particulate phase. Given the difficulties listed above in studying sorption under environmental conditions, it is thus important to investigate the effect(s) of different experimental conditions on the resulting log Kd (particle-water partitioning

coefficients), which will allow one to optimize the conditions best suited to study the process of sorption of a particular colloidal phase, and to minimize the presence of colloidal impurities. Often studies are carried out at higher actinide concentrations in order to minimize colloidal effects. The results are then extrapolated to orders of magnitude lower concentrations, yet, the complexation and sorption behavior of actinides or trace metals (Buffle, 1990), is often concentration dependent, and thus, such extrapolations should be viewed with caution. Concentration dependency is also observed in the production of Pu(V) tracer by the solvent extraction and photoreduction of Pu(VI) of Saito et al., 1985, which poses additional challenges when attempting to produce Pu(V) tracers at pM and fM concentrations.

Since the goal of many actinide studies is to determine the effects of additional solutes (e.g., organic molecules) onto mineral matter, it is important to minimize colloidal impurities, so that the specific interactions can be isolated. The goal of this study is therefore to investigate the optimal conditions, which minimize the introduction of colloidal impurities into the experimental systems when studying particle-water interactions of actinides at near-ambient pM and fM concentrations. Special procedures that were investigated for particle-water separation, included cleaning from impurities, and attainment of neutral conditions for sorption experiments.

2.3 Methods

All sorption experiments were carried out in batch fashion, using 50mL centrifuge tubes as the batch reactors. All components of the system were pipetted. The pH of each tube was measured and then placed on the shaker for 2 days. Once removed from the shaker, the pH was measured again and the tube was centrifuged (2700 x g), or filtered through a 0.45μm filter, depending on experiment. The supernatant or filtrate was decanted into a Millipore stirred cell ultrafiltration setup containing a 1kDa ultrafilter. The 50mL sample was ultrafiltered to a retentate volume of 5mL for a concentration factor of 10. The three fractions: the silica particles that were centrifuged or filtered out (particulate), the fraction retained by the ultrafilter (retentate or colloidal) and the fraction that passed through the ultrafilter (permeate), were counted by Liquid Scintillation Counting (LSC) for Th or was processed by anion exchange columns and counted by alpha spectroscopy for Pu.

For Pu, on the order of 10 dpm (=10^{-13} moles) of ^{240}Pu were added to each experiment, while in the case of ^{234}Th, 10,000-100,000 dpm, equivalent to 1 to $10x10^{-15}$ moles, were used in 50 ml, resulting in about 2 and up to 0.2 pM concentrations of Pu and Th, respectively.

Because reagents can also introduce colloidal ligands at concentrations of the order of 10^{-9}M, thus creating opportunities of artificial "pseudo-colloid" formation of the tracer that is originally present in ionic form, it might be important to clean-up all reagents that are used.

In order to provide results that more accurately portray ambient conditions in the aquatic environment, and to gain the capability to discern differences in experimental treatments, it is important to minimize potential artifacts from colloid introduction by reagents and pre-neutralization of tracer.

The goal of the methodology study is thus to find the optimal conditions under which sorption of actinides to silica particles in the presence of a (experimentally added, or naturally present) colloidal third phase can be investigated. The following conditions were investigated in great detail: 1) modes of separation of particles (≥0.4μm) from colloids (0.45μm to about 1nm), and low-molecular weight species (≤1kDa ≈ 1nm); 2) purity of acids that were used; 3) types of containers used for tracer storage, i.e., glass vs. teflon; 4) ways how neutral pH conditions are established in solution, i.e., pre-neutralization of a tracer that is only stable under strongly acidic conditions, or using buffers; 5) preparation of low-molecular forms of tracer at neutral pH through ultrafiltration of pre-neutralized tracer; 6) pre-treatment of silica surface; 7) purity of reagents being used in terms of presence of colloids.

The importance of the above listed conditions was assessed through their effects on values of the particle-water partitioning coefficient, Kd. Kd can be calculated from the fraction of the activity in the particulate (fp), colloidal (fc) and dissolved (fd) fractions, and the particle concentration (Cp), i.e.,

$$Kd = fp/\{(fc+fd)*Cp\}$$

In order to better assess the colloidal contribution to particle-water partitioning, the partitioning coefficient (Kd_c) was also calculated by including the colloidal

fraction in the particulate fraction, i.e., that fraction that is retained by an ultrafilter, i.e.,

$$Kd_c = (fp+fc)/\{fd*Cp\}$$

Where fp = fraction on the particles (e.g., silica); fc = fraction retained by 1kDa ultrafilter (retentate); fd = fraction that passes through a 1kDa ultrafilter (permeate); Cp = particle concentration (g/mL); Kd = particle-water partitioning coefficient; Kd_c = particle & colloid-water partitioning coefficient including the retentate in the particulate fraction.

2.4 Results and discussion

The method of separation, filtration or centrifugation, showed a very significant effect on the log Kd and log Kd_c values in experiments investigating the partitioning of thorium and plutonium onto silica particles. Filtration consistently resulted in higher values (Figure 2.1), which appears to be the result of trapping the colloids onto filters, thus biasing the particulate fraction. While it is well known that in the presence of colloids, filtration can artificially collect "sticky" colloids (Buffle, 1990) it appears that heavier and stickier colloids can also affect centrifugation results under conditions when unpurified, reagent-grade NaOH or $NaHCO_3$ is used. Filtration is one of the most common means for particle/water separation that is used for traditional particle water partitioning coefficient determinations and is also employed in field measurements. However, if the purpose of the study is minimize the effects of

colloidal components of the system, centrifugation is clearly the better choice for particle separation.

Results from a comparison of the ^{234}Th tracer prepared with trace metal vs. reagent grade acid, or stored in Teflon vs. glass for 30 days, indicate that there was little difference between the two grades of acid. Their log Kd values were 4.62 ± 0.08 vs. 4.47 ± 0.08 for trace metal acid and reagent grade, respectively (Appendix B). For storage in teflon vs. glass containers, the log Kd value was higher in Teflon (4.9 ± 0.03) than that stored in glass (4.0 ± 0.03). Their respective log Kd_c values were 5.01 ± 0.1 and 5.03 ± 0.1 (Table 2.1). ^{240}Pu tracer showed no difference in log Kd nor log Kd_c values when stored in glass or Teflon vials for over 30 days (Table 2.1). However, while the log Kd_c values for Th showed no difference between the storage containers, the Kd values for Th were significantly higher than those for Pu, suggesting different colloidal carrier phases for the two elements.

Of all the treatments assessed here, treatment of the acidic tracer in a neutral solution seems to have the biggest effect on log Kd values (Table 2.2). While pre-neutralization of Th and Pu with sodium bicarbonate resulted in a log Kd value (4.32 ± 0.08 and 4.7 ± 0.05, respectively) that was not much different from the acidic tracer added to a buffered solution (4.39 ± 0.08 and 4.7 ± 0.08). The log Kd_c value was significantly larger for the bicarbonate-neutralized Th tracer, indicating a larger colloidal contribution. However, the similarity in Kd values between buffered and bicarbonate-neutralized tracers strongly suggests that carbonate complexation of Th(IV) and Pu(IV) was not a major factor in

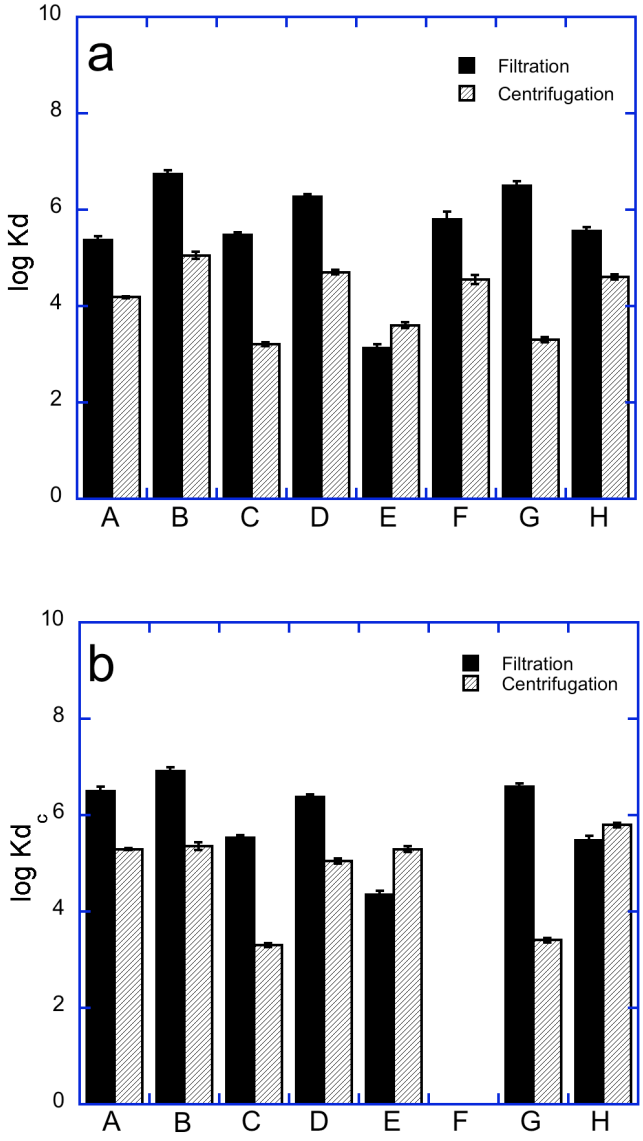

Figure 2.1. Comparison of log Kd and log Kd_c values calculated different tracer (Th or Pu) treatments on silica when separated by filtration (solid) or centrifugation where the treatments are as follows: A)Th in Tris/HCl, B) Pu in Tris/HCl, C) Pu-NaOH neutralized, D) Pu-NaHCO3 neutralized, E) Th-NaOH neutralized and pre-ultrafiltered, F) Th-NaHCO3 neutralized and pre-ultrafiltered, G) Pu-NaOH neutralized and pre-ultrafiltered, H) Pu-NaHCO3 neutralized and pre-ultrafiltered,

Table 2.1
Comparison of Log Kd and log Kd_c values of $^{234}Th(IV)$ and $^{240}Pu(IV)$ tracers stored in glass versus Teflon containers and 0.5g/L silica; 0.1M $NaClO_4$/ 50mM Tris/ 25mM HCl equilibrated for 2 days.

ID	Log Kd	±	Log Kd_c	±	Mass Balance	±
Th- in teflon	4.9	0.03	6.5	0.3	60	5
Th- in glass	4.0	0.03	6.6	0.3	63	0.6
Pu- in teflon	4.7	0.08	5.0	0.2	106	8
Pu- in glass	4.7	0.08	5.4	0.2	109	8

determining particle-water partitioning. However, the sodium hydroxide pre-neutralized tracer showed order of magnitude lower log Kd and log Kd_c values, i.e., 3.6 ± 0.07 and 5.27 ± 0.7 for Th; 3.2 ± 0.04 and 3.3 ± 0.04 for Pu. This is likely indicating the presence of hydroxyl species that are not particle active and that can pass through the 1kDa filter, ending up in the permeate fraction, thus resulting in lower particle water partitioning values. However, the Th tracer shows a larger increase in the log Kd_c values when NaOH pre-neutralized, indicating formation of extra, but less-interactive, colloids. Thus, the increase in the log Kd_c values, and concomitant lowering in Kd values, indicates that these extra colloids were less surface active.

Table 2.2
Comparison of log Kd and log Kd_c values with $^{234}Th(IV)$ and $^{240}Pu(IV)$ tracers added in a buffered (Tris/HCl) solution versus pre-neutralized with NaOH or $NaHCO_3$ to pH ~7; silica at 0.5g/L, in 0.1M $NaClO_4$

ID	Log Kd	±	Log Kd_c	±	Mass Balance	±
Th in buffer solution	4.39	0.08	5.99	0.09	68.24	0.12
Th-NaOH neut.	3.60	0.07	5.27	0.07	66.07	0.11
Th-NaHCO3 neut.	4.32	0.08	6.63	0.09	72.36	0.12
Pu in buffer solution	4.7	0.08	5.0	0.2	106	8
Pu- NaOH	3.2	0.04	3.3	0.04	58.3	2.6
Pu-$NaHCO_3$	4.7	0.05	5.04	0.07	48.7	2.6

In order to eliminate the colloidal forms that pre-neutralization can produce in the tracer, the pre-neutralized tracer solutions were pre-ultrafiltered and compared to the case of an acidic tracer added to a pre-ultrafiltered buffered solution. Figure 2.2 showed the percent sum of fractions of the pre-ultrafiltered tracers found to be retained by the ultrafilter (3kDa for pre-neutralized tracers and 1kDa for buffered solution). For sodium hydroxide neutralization 51% of the ^{234}Th was retained, while for Pu, it was 17 %; furthermore, 28 and 60% of the Th and Pu, respectively, that passed through the filter. In one experiment (results not shown) in which the Pu was first neutralized to pH 10 and then back titrated to pH 6.7, results showed an even higher percentage of Pu retained by the ultrafilter (87%), indicating the irreversible formation of hydroxy species of Pu. In the case of sodium bicarbonate used to pre-neutralize the tracers, the colloid-water pa looked similar for both Th and Pu, i.e., 26% and 22%, were retained, less than 2% sorbed onto the ultrafilter, and 71% and 76% passed through the filter. For the case of an acidic tracer being added to a buffered

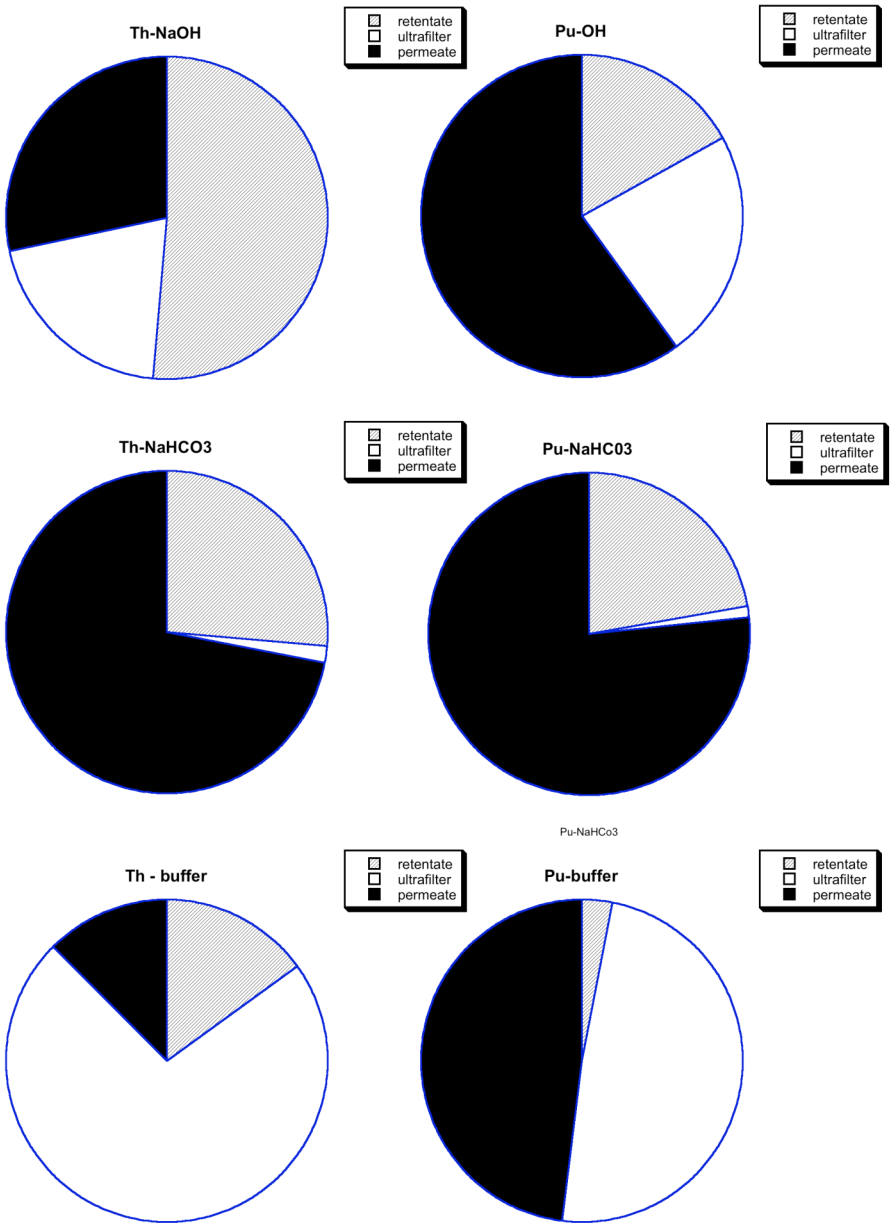

Figure 2.2. Mass balance (% total as sum of fractions) of pre-neutralized, pre-ultrafiltered thorium and plutonium tracers. NaOH and $NaHCO_3$ neutralized tracers ultrafiltered with a 3kDa ultrafilter and the tracers in buffer (Tris/HCl) solution were ultrafiltered with a 1kDa ultrafilter

(Tris/HCl) solution and subsequently passed through a 1kDa ultrafilter, very little of the tracer was retained as a colloidal actinide in either case (15% for Th, and 3% for Pu). The biggest difference between the buffered solution and the pre-neutralization was in the fraction that was lossed on the ultrafilter. Since less than 10% loss to the ultrafilters was observed in sorption experiments to silica particles (Roberts et al., submitted) one might conclude that the addition of an acidic tracer to a buffered solution results in a tracer whose behavior more closely resembles that in a ionic form. Thorium(IV) and Pu(IV) are both known to be particle reactive, and when tracers only are used, they seem to sorb more strongly onto the ultrafilter. This is also confirmed by the mass balances, whereby it was always higher in the presence of silica particles than in the absence of silica. In order to test the speciation of the tracers retained on the ultrafilters, i.e., if sorbed as an ion, or coagulated in a colloidal form, the tracer was subsequently diafiltered (i.e., washed through with extra water) (results not shown). The fact that only a minor fraction of the tracer could be washed through the ultrafilter, and the tracer associated with the filter remained large, suggests that the tracer is present in a colloidal form at neutral pH. Interestingly, the fraction of the tracer that was observed on the filter was only significant in experiments with the tracer alone, but was found insignificant in experiments where particles were present.

The partitioning experiments for thorium showed significantly higher log Kd values for the pre-ultrafiltered tracer, pre-neutralized with $NaHCO_3$ (4.55 ± 0.09), leading one to believe that the colloids generated from the neutralization

process to some extent lowered their reactivity with the particle surfaces (Table 2.3). Also for thorium, the log Kd_c values were significantly enhanced under pre-neutralized tracer conditions, indicating that when low molecular weight tracer was added, there was still a strong association of the tracer with a colloidal fraction. In the case of sodium bicarbonate, the colloid association was so strong that there was no measurable activity in the permeate and a log Kd_c value could not be calculated.

Table 2.3
Log Kd and Log Kd_c values to silica (0.5g/L) for pre-ultrafiltered, colloid free tracer for ^{234}Th(IV) and ^{240}Pu(IV). Acidic tracers were added to buffer solution (Tris/HCl) and pre-ultrafiltered (1kDa) and pre-neutralized tracers were pre-ultrafiltered (3kDa) and added to unbuffered solution. All solutions were 0.1M $NaClO_4$.

ID	Log Kd	±	Log Kd_c	±	Mass Balance	±
Th in buffer solution: <1kDa	4.18	0.02	5.29	0.12	[b]	
Th- NaOH neutralized; <3kDa	3.6	0.06	5.29	0.4	72.0	7.0
Th-$NaHCO_3$ neutralized; <3kDa	4.55	0.09	[a]	[a]	71.8	9.5
Pu in buffer solution; <1kDa	5.05	0.08	5.35	0.13	[b]	
Pu-NaOH neutralized; <3kDa	3.30	0.05	3.40	0.05	88.7	5.6
Pu-$NaHCO_3$ neutralized;<3kDa	4.60	0.05	5.79	0.11	104	6.4

[a]no measurable activity in permeate; [b]not quantifiable.

In the case of plutonium, sodium hydroxide neutralized, pre-ultrafiltered tracer also showed a lower log Kd value than for thorium (3.3 ± 0.05). This again is likely a result of the formation of hydroxy species that pass through the ultrafilter in the partitioning experiments but appear to be less surface active, thereby lowering the association with particles. Unlike thorium, the plutonium did not show as much of an increase in the log Kd_c in the buffered solution or

with sodium hydroxide, but an enhancement was seen in the case of sodium bicarbonate.

The presence of colloidal impurities of different surface reactivities, either pre-existing or newly introduced into the system, biasing the results, can explain the apparent inconsistencies in the data. This is true for both traditional particle water partitioning coefficients, and assessments of the colloidal fraction. Fortunately for environmental radiochemistry experimentation, many of the attempts to clean or pre-treat the experimental system to remove colloidal impurities yielded results that showed little difference between the comparisons. For example, pre-cleaning of the silica particles was expected to remove any colloidal particles as well as provide a fresh clean surface for sorption. While there was some evidence that there were some different colloidal particles present, there was no significant effect seen in the log Kd values when using acid cleaned (4.4 ± 0.09) or uncleaned (4.61 ± 0.1) silica particles. However, a significant difference was seen in the log Kd_c values, i.e., 5.81±0.09 vs 6.20 ± 0.10, indicating a slightly higher (but "non-sticky") colloidal fraction for the silica that was not cleaned. Likewise, colloidal impurities were expected from the reagents used for the test solution (0.1M $NaClO_4$, 50mM Tris, 25mM HCl), yet attempts to clean this solution by passing through chelex and XAD-8 columns or pre-ultrafiltration of this solution showed no effect on log Kd or log Kd_c values (Figure 2.3). Yet, unlike the case for Th, Pu showed a difference in the mass balance with no pre-treatment as compared to any of the pre-treatments. With no pre-treatment, the mass balance (43.9%) was over 20%

less than any of the experiments that were pre-treated (67.1 – 69.5%), indicating the main effects occurred on the container-wall sorbed fraction. However, in a separate experiment, from the fraction that was sorbed to container walls for both Th and Pu tracers, <10% was released into a tracer-free solution (not shown).

2.5 Conclusions

Seven experimental conditions were tested to determine the effect they had on the resulting particle water partitioning coefficients (log Kd and log Kd_c) of thorium and plutonium on silica particles. Most conditions, such as the grade of acid used for the tracer, pre-cleaning of silica particles and pre-cleaning of experimental solutions, showed a negligible effect on the resulting log Kd values. However, significant differences were seen in the values of log Kd_c, the particle-water partitioning coefficient that includes the colloidal fraction as part of the particulate. Regardless, if a study is focused on a ternary system investigating the effects of a colloidal organic fraction on sorption reactions, cleaning and/or pre-ultrafiltration of all reagents, which reduce the presence of colloidal impurities, is still recommended as a precautionary measure.

The method of particle separation by filtration vs. centrifugation, resulted in highly significant differences in the resulting log Kd values. While the separation method used should depend on the objective of ones study, if the purpose of the study is to determine effects of differing experimental solution

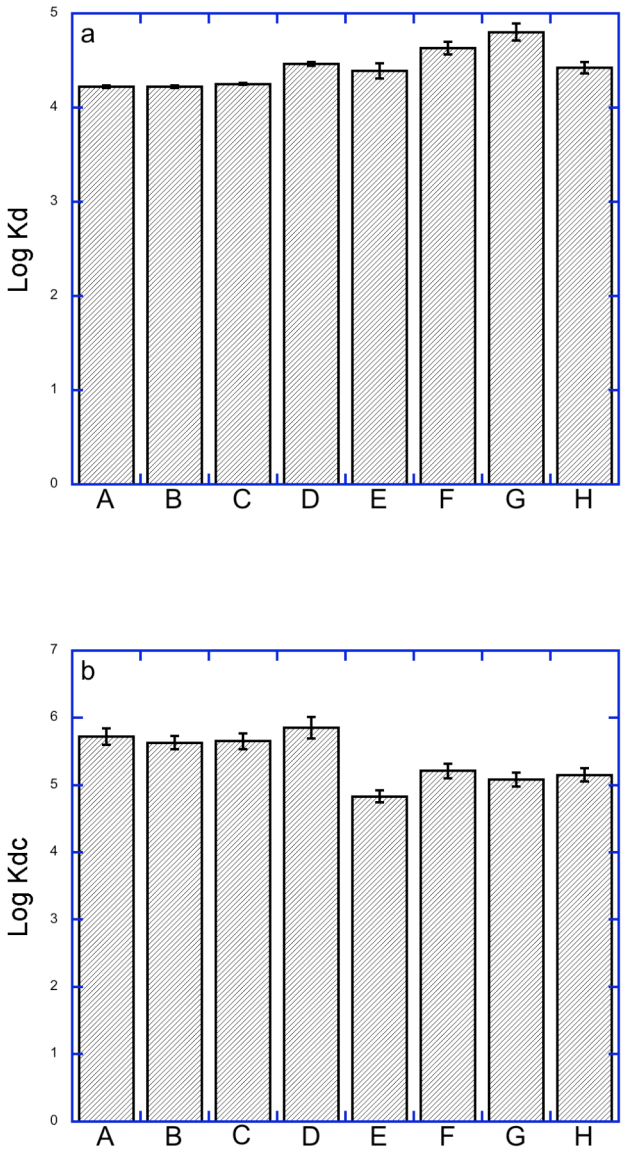

Figure 2.3. Comparison of solution (0.1M $NaClO_4$ 50mMTris/25mMHCl) pre-treatment on resulting a) log Kd and b) log Kd_c values for ^{234}Th and ^{240}Pu to silica (0.5g/L). Pre-treatments included: A.Th- none, B.Th- columns (through Chelex and XAD-8), C. Th- pre-ultrafiltration (<1kDa) of solution, D. Th- columns and pre-ultrafiltration, E. Pu- none, F. Pu-columns, G. Pu- pre-ultrafiltration, and H. Pu- columns and pre-ultrafiltration.

conditions in which changes to the colloidal fraction are important, centrifugation is clearly the better method of separation.

By far the greatest impact on the results was the pretreatment of the acidic tracers to produce a near neutral experimental system. Pre-neutralization by NaOH, by far the most common method cited in the literature, showed a definite propensity toward formation of non-surface reactive colloidal complexes for both Th(IV) and Pu(IV), resulting in significantly lower log Kd values, compared to pre-neutralization by $NaHCO_3$, or addition of an acidic tracer in an solution with an inert buffer. Given that the mass balance of the pre-neutralized tracers clearly showed a strong colloidal component, we recommend that inert buffers be used to best assess the behavior of an ionic tracer with a tendency for "pseudo-colloid" formation.

The results of these experiments are relevant not only for experimentalists, but also for modelers as well. Any model that attempts to predict that sorption or transport of Th(IV) or Pu(IV) at fM to pM concentrations will need to take into account the presence of colloidal forms of these tracers in solution and on surfaces.

3. Pu(V) REDUCTION AND ENHANCEMENT OF PARTICLE-WATER PARTITIONING BY EXOPOLYMERIC SUBSTANCES

3.1 Overview

Central to understanding the environmental behavior of Pu in vadose- and saturated-zones, as well as waste streams, is the contribution of exopolymeric substances (EPS) from microbial communities and other forms of colloidal natural organic matter (NOM) to Pu speciation. Because Pu(V) and Pu(IV) are present in aquatic systems at sub-pM concentrations, many established techniques for chemical speciation and oxidation state determination are not available. However, the two redox states of Pu can be distinguished through their tendency to form colloidal species. In controlled experiments, using low-colloid reagents that had been pre-cleaned by passing through chelex and XAD resins to remove trace elements and trace organics, we investigated the ability of NOM compounds to: 1) reduce Pu(V) to Pu (IV) (as determined by % colloidal ≥1kDa); 2) enhance particle- (or colloid-) water partition coefficients to silica particles, i.e., Kd (and Kdc); 3) affect the results of the reaction sequence of tracer addition to the solution containing silica particles and NOM compounds in a buffered inert electrolyte.

The reduction of Pu(V), as evidenced by a large colloidal fraction (≥ 1kDa), was fast (1day) with hydroquinone and humic acid, and slower (2 weeks) for EPS from *Pseudomonas fluroescens* Biovar II. Pu(V) alone did not form colloidal species. Results from an experiment investigating Pu(V) uptake by 5 μm silica particles in 0.1M $NaClO_4$ in a Tris buffer solution, and in the presence

or absence of EPS, indicate that Pu(V) requires about a month for the particle- or colloid-water coefficients (Kd and Kc, respectively) to reach a quasi-equilibrium state. Kd and Kc values after 30 days of equilibration were then close to those of Pu(IV), which reached equilibrium within 1 day. When Pu(IV) was added to silica particles first, before the NOM compounds (i.e., humic acid or EPS) was added, the resulting Kd values were always higher than when Pu(IV) was added to the organic substances first this indicates that the sorption reactions to silica are, at least in part, irreversible. In all experiments, regardless of being present as either Pu(V) or Pu(IV), Pu became significantly associated with colloids ≥ 1kDa, except in the case of pure Pu(V) solutions. While the association of the different organic colloids with silica particles was relatively small, their particle-reactivity was likely related to their amphilicity. Pu migration in the subsurface might thus become controlled, at least in part, by the surface activity of the colloidal carrier molecules.

3.2 Introduction

Plutonium, and anthropogenic radionuclide, has been introduced into the environment via the atmosphere from nuclear weapons testing and locally in soils and surface waters from accidental releases from nuclear weapons production and reprocessing facilities. Plutonium concentrations in natural aqueous systems, derived from atmospheric testing, are on the order of femtomolar, while accidental release to unrestricted environments can be larger by many orders of magnitude. Maximum contaminant levels (MCLs) are

currently 10^{-12} M (EPA). Such environmentally relevant concentration levels pose a number of challenges when trying to understand the phyical chemistry of environmental Pu.

The chemistry of plutonium in aquatic environments can, in principle, be quite complex, as Pu has the ability to exist in multiple oxidation states (III, IV, V, VI). However, normally in aquatic systems, only two oxidation states of Pu have to be realistically considered: IV and V. In aquatic systems with low organic matter concentrations, the more soluble Pu(V) dominates (Choppin and Wong, 1998; Choppin, 2003; Choppin and Morganstern, 2001) while in systems with higher organic matter concentrations, the more particle reactive Pu(IV) prevails (Choppin and Wong, 1998; Choppin and Morganstern, 2001). The redox potential for the Pu(IV)/Pu(V) couple is +0.17V at pH=0, +0.70±0.12 at pH=8, and +0.52±0.24V at pH=14 (Allard et al., 1980; Choppin 1983, 2007; Choppin et al., 1997) suggesting that, in oxygenated aquatic systems with low organic matter concentrations, Pu(V) should be the thermodynamically stable oxidation state.

Recent work at the Rocky Flats Environmental Technology Site demonstrated that plutonium in streams and pond discharges occurs as Pu(IV) and is closely bound to negatively-charged colloidal macromolecular organic compounds and iron (OC) compounds such as humic acids but not by acid polysaccharides that are principal components of extracellular polymeric substances (EPS) produced by bacteria (Santschi et al., 2002). An obvious question to ask is how different types of natural organic matter (NOM), such as

humic acids and EPS, affect mobility and sorption of Pu in soil and groundwater systems.

Because the oxidation state of Pu is likely regulated not only by concentrations but also types of organic matter, the ultimate fate of Pu in the aquatic environment might depend on factors that regulate microbial activity (and therefore the production of organic matter), such as nutrient status. Furthermore, EPS excreted by different bacteria species could have different abilities to reduce Pu(V) to Pu(IV). In this paper, we therefore compared not only EOS form different microbial species, but also different commercially available organic compounds (e.g., humic acid, hydroquinone, and glucose), which, according to thermodynamic calculations based on published redox potential, could also have the ability to reduce Pu(V) to Pu(IV). An additional attribute is their compositional similarities with EPS. EPS, like humic acid, contains functional groups such as carboxyl, hydroxyl, phenolic an quinone groups that are contained in a complex mixture of compounds such as acid polysaccharides, proteins and lipids at different stages of degradation.

One of the aims of this work is to test a series of model compounds which have the potential to reduce Pu(V) and to then compare the reduction potentital of these compounds with EPS. Reduction ability is defined and assessed by the relative ability of the compound to foster Pu sorption onto particles such as silica (SiO_2(s)). Since Pu, in the aquatic environment is legally regulated well below pM concentrations, environmentally relevant experiments have to be conducted at pM or lower concentrtation. More common concentrations are on

the order of μM to mM (Hongxia et al., 2006; Kumar et al., 2006; Saito et al., 2005, Geibert and Usbeck, 2004). Conducting experiments at environmentally relevant conditions poses a logistical challenge because of the presence of colloidal impurities. Such impurities originate from reagents and during pre-neutralization (e.g., with NaOH; (Hongxia et al., 2006; Kumar et al., 2006; Saito et al., 2005, Geiberts and Usbeck, 2004)) of the acidic tracer through the formation of irreversible hydrolysis products.

In our study, we attempted to minimize potential artifacts form colloid introduction by reagents and pre-neutralization of tracer, in order to provide results that more accurately portray ambient conditions in the aquatic environment, and to gain the capability to discern differences in experimental treatments. For example, in surface and subsurface waters, elemental ratios of dissolved or particulate Pu to its carrier-phases organic carbon (OC) or Fe are never higher than $1:10^{-6}$, not even in contaminated areas, but more often closer to $1:10^{-9}$ given average concentrations for R-COO- (organic acid), Fe and Pu near 10^{-6}, 10^{-7}, and 10^{-15} M, respectively. At these low Pu concentrations, any complexing and/or colloidal impurities in the experimental system can influence the results in uncontrollable and unpredictable ways, whereas at mM and μM concentrations of Pu this would not be the case. However, at such elevated Pu concentrations, only the weakest binding sites would be studied, which have little relevance for our understanding of the natural environment.

Reagents can introduce colloidal ligands at concentrations of the order of 10^{-9} M, thus creating opportunities of artificial "pseudo-colloid" formation of the

tracer that is originally present in ionic form. For example, pre-neutralization of acidic Pu(IV) (or Th(IV) tracer using NaOH or $NaHCO_3$, as opposed to using a Tris/HCl buffer, can yield log Kd values that are different by 1-2 orders of magnitude (Section 2).

Plutonium speciation and mobility can be affected to a great extent by NOM. Amphiphilic NOM molecules can act as surfactants or emulsifiers, depending on their molecular weight. Surfactant solubilize more hydrophobic particles and colloids in water by producing negatively charged, low molecular weight and more hydrophilic adducts and/or micelles, while emulsifiers embed more hydrophobic particles or colloids in a high molecular weight matrix that clings to or coats particles or colloids. This changes their (negative) surface charge and thus enhances their solubility in the aqueous phase by rendering the adduct to become more hydrophilic. Humic acids (HA), rich in negatively charged carboxylic acids and aromatic carbon rich compounds, and with molecular weights of a few kDa, can act as surfactants, while polysaccharide and protein-rich exopolymeric substances (EPS), with molecular weights of 10s to 1000s of kDa, can act as emulsifiers, as both of them are amphiphilic. The amphiphilicity is, to a large extent, due to the more hydrophobic aromatic moieties in both, in EPS mostly due to proteins and lips.

NOM not only contains amphipiles but also redox active molecules such as hydroquinones. It is thus of interest as to how NOM fractions, e.g., HA and EPS from different microorganisms, affect particle-water partitioning and redox

properties of Pu in model systems containing silica particles (as proxies for soil minerals) and representative NOM molecules.

3.3 Methods

3.3.1 Sorption studies

Sorption studies were carried out in batch experiments using conditions to mimic those found in the environemtn; near neutral pH, sub-pM concentrations of plutonium, 0.5g/L inorganic particles and 5mg/L organic molecues, e.g., colloidal biomolecules. To minimize the effects of colloidal impurities, plasticware and silica particles were cleaned with 1M HCl, triple rinsed with deionized water and pre-conditioned with the test solution (0.1M $NaClO_4$/50mM Tris/25mM HCl). Details of experimental results comparing different solution conditions that are typically used in the literature can be found in Geibert and Usbeck (2004). The test solution was pre-cleaned by passing the solution through columns containing chelex and XAD-8 resins to remove trace metal and organic impurities respectively. The chemically inert buffer (Tris) was used to maintain environmentally relevant pH while minimizing formation of colloidal species of the plutonium tracer itself. Silica particles used were purchased from EM Science and had a mean diameter of 5μm and a surface area of 500m^2/g, suggesting a large porosity.

The ^{240}Pu tracer used was purchased form Isotope Products Laboratory and was assumed to be in the IV oxidation state as the tracer was in 4M HNO_3. This was confirmed through oxidation state determination procedure from Saito

and Choppin (1985) in which ≥75% of the tracer was measured in the IV fraction. Up to 20% was measured on the interface which could also partially or largely be IV (Appendix B). Pu(V) was made from a dilution of this tracer following a modification of the procedure of Saito et al. (1985). Briefly, ^{240}Pu(IV) tracer was oxidized with potassium permanganate in the dar overnight to Pu(VI). The following day, the newly formed Pu(VI) was extracted into an organic solution (0.5M TTA in cyclohexane), followed by immediate reduction to Pu(V) and its back extraction into the aqueous phase in 0.1M sodium acetate at pH=4.7. Because the kinetics of Pu are dependent on the Pu concentration in complicated ways, producing optiumum yields at particular concentration-dependent times, and because the Pu concentration that we used were many orders of magnitude lower than those used by Saito et al., (1985), reduction under fluorescent light inititally did not produce the desired results. Instead, only the reduction of Pu(VI) to Pu(V) in the dark, carried out in as short a time as possible (seconds), allowed the recovery of about 10% of the original concentration. Another modification was the use of TTA directly from the bottle rather than in a purified form, as the TTA direct from the bottle was more readily dissolved and resulted in higher Pu recoveries.

On average, 81.1±2.3% (n=4) of the Pure (V) tracer was found in the permeate and 3.5±0.6% in the colloidal (i.e., retentate) fraction (after 1kDa ultrafiltration followed by diafiltration) thus providing evidence for the low molecular nature of this tracer. In contrast 45±4% and 47±4% of the pure Pu(IV0 tracer were found initially in the retentate and permeate fractions respectively,

with the retentate fraction increasing, and the permeate fraction rapidly decreasing with time (Figure 3.1). Overall recovery of Pu(IV) dropped form 97% (t=0.04d) to 50% for t>6d. These results support the proxy use of colloidal vs. low molecular weight fraction for Pu(IV) and Pu(V), respectively, especially in short-term experiments.

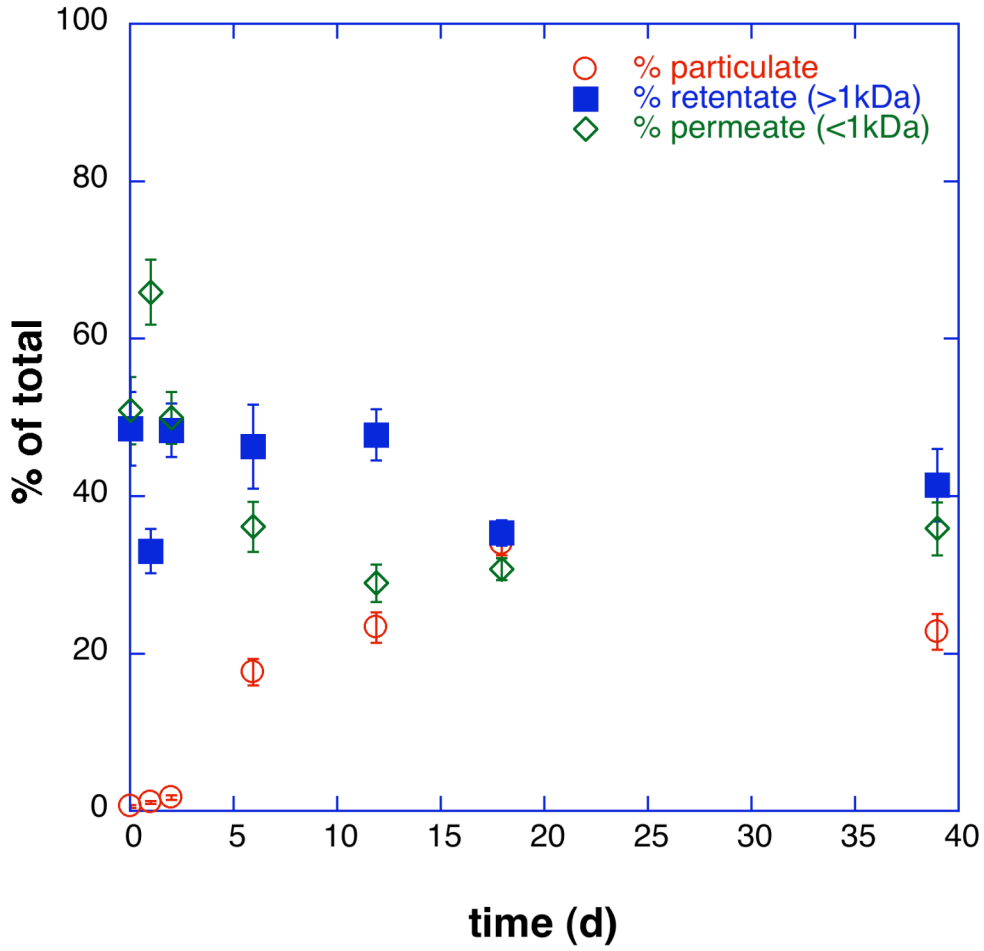

Figure 3.1. Colloid aggregation kinetics of pure Pu(IV) tracer. Size fractions of Pu(IV) tracer alone as a function of time where the % in each fraction is a percentage of the sum of the measured fractions.

For the batch system adsorption experiments, the reagents were added by pipetting the test solution into the centrifuge tube, which contained silica where applicable, followed by the organic colloid to which the plutonium tracer was added last. Tubes were shaken and the pH was determined prior to placement on the shaker table.

EPS were isolated from bacterial (and phytoplankton) cultures by a series of ethanol precipitation, diafiltration, and lyphilization steps, as described by (Hung et al., 2005). Cultures of soil (*Pseudomonas fluorescens* Biovar II) and estuarine (*Sagittula stellata*) bacteria, as well as marine phytoplankton (*Synecococcus, Skeletonema costatum* and *Emiliani huxleyi*), were utilized.

The batch system was placed on a benchtop shaker (Barnstead) for the prescribed amount of time, which was initially two days, based on Th(IV) sorption kinetics. The tubes were then removed and the pH measured again to make sure no significant drift occurred. At this point, the batch experiments were ready for size fractionation. First, the tubes were centrifuged (2700 x g) for 5 minutes to settle out the silica particle. The supernatant was decanted into a Millipore stirred ultrafiltration cell utilizing a 1kDa filter to separate the >1kDa (retentate or colloidal fraction) from the <1kDa (permeate or truly dissolved fraction). After separation, concentrated nitric and hydrochloric acids were added along with 242Pu(IV) tracer. Samples were evaporated to dryness, reconstituted in nitric and hydrochloric acids, evaporated again, reconstituted in hydrochloric acid, evaporated and finally redissolved in 75mL 9M HCl for

plutonium separation via ion exchange columns. Once the plutonium separation was complete, samples were precipitated using lanthanum fluoride onto a 0.2μm filter and counted by alph spectroscopy (Joshi, 1985).

3.3.2 Calculation of particle-water partition coefficients

Distribution coefficients are empirical parameters that express the partitioning of a target sorbate between 'dissolved' and 'particulate' phases. In this case, we consider three phases: 1) particulate (particles removed through centrifugation); 2) colloidal material (>1kDa but not removed through centrifugation); 3) dissolved (<1kDa). The partitioning parameters are defined as follows:

Particulate = silica: $Kd = fp/((fc+fd)*Cp$

Particulate = silica + retentate: $Kd_c = (fp+fc)/(fd*Cp)$

Particulate = retentate: $Kc = fc/(fd*Cp)$

Where fp = fraction on the particles; fc = fraction retained by 1kDa ultrafilter (retentate); fd = fraction that passes through a 1kDa ultrafilter (permeate); Cp is the particle (or colloids) concentration (g/mL); Kd = particle water partitioning coefficient (traditional); Kd_c = particle-water partitioning coefficient including the retentate in the particulate; Kc = colloid-water partitioning coefficient;

The error in the Kd (Kd_{err}): $Kd*sqrt(((fp_{err}/fp)^2+((fc+fd)_{err}/(fc+fd)^2)$

OR $Kd*sqrt((fp+fc)_{err}/(fp+fc)^2+((fd)_{err}/(fd)^2)$

Log Kd_{err} was calculated for both log ($Kd+Kd_{err}$) and log ($Kd-Kd_{err}$); because these values are low (generally <0.10), and log ($Kd-Kd_{err}$) is the larger of the two

errors, the latter value was used in all of the tables and plots as both the "+" and "-" error.

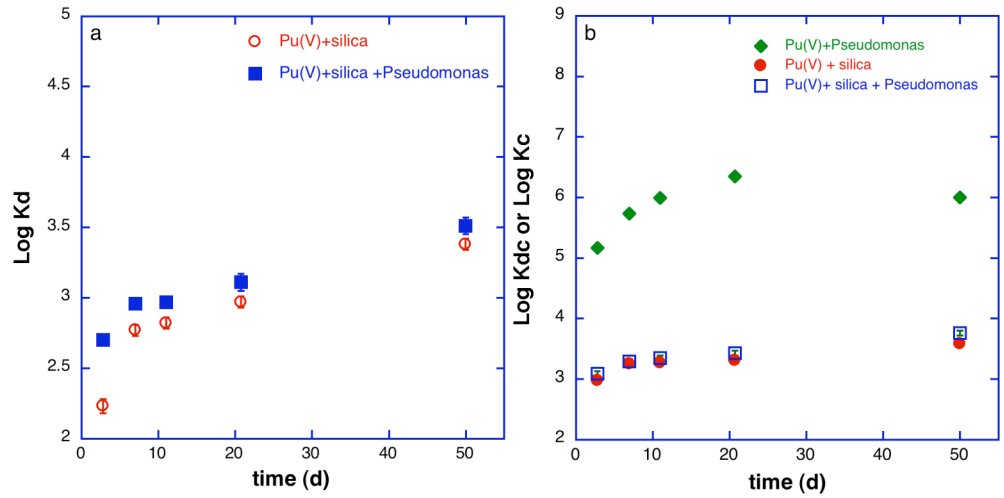

Figure 3.2. Kinetics for ternary sorption system of Pu(V), silica particles and extracellular polymeric substance (EPS) from *Pseudomonas fluroescens* Biovar II. a) log Kd values b) log Kdc or Kc values

All fractions (fp,fc,fd) were calculated based on the sum of the fractions recovered. The most significant loss of plutonium tracer occurred in the abasence of silica, e.g., when organic colloids, alone were present. Recoverability of the plutonium "lost " to the container walls was assessed by conducting a 2 day sorption test using a binary system of colloids, which was then followed by a ternary (silica, organic colloid, and plutonium) sorption test experiment. Four organic compounds: humic acid, hydroquinone, glucose and EPS from Pseudomonas fluorescens Biovar II a common soil bacteriaum, were

systematically tested in this regard. The recoverable plutonium fraction was very low, with the highest value being 11% of the "lost" fraction, while the other 3 tests gave values that were less than 10%. Therefore, the lost fraction did not need to be considered further in calculations. Therefore, the sum of the measured fractions that was used here most accurately represents the partitioning of plutonium.

Table 3.1
Comparison of Particle-water partitioning coefficiencts log Kd (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp)) for Pu(V) to silica under light and dark conditions to ensure that photoreduction does not contribute to reduction.

Treatment	Time (day)	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total)
LIGHT								
Pu(V)+Si	49.99	3.38	0.04	3.58	0.05			86
Pu(V)+Pseud	49.99					6.0	0.06	63
Pu(V)+Si+ Pseud	49.99	3.51	0.05	3.76	0.04			90
DARK								
Pu(V)+Si	50.96	3.28	0.04	3.47	0.04			88
Pu(V)+Pseud	50.96					6.0	0.05	71
Pu(V)+Si+ Pseud	50.96	3.45	0.03	3.66	0.03			62

[a] log Kc of 6 is equivalent of 83% in colloidal form, given an EPS concentration of 5 mg/L.

3.4 Results

Results of studies of the kinetics of Pu(IV) and (V) partitioning to a) silica particles, b) EPS from *Pseudomonas fluorescens* Biovar II, and c) silica and EPS are shown in Figures 3.2 and 3.3. Pu(V) sorption kinetics seem to be slower than that of Pu(IV): there is a continuous increase, albeit slight, during the 50 days of equilibration, without clearly reaching a plateau in the case where silica particles were present. In case b, Pu/EPS, in contrast, a plateau is reached after 20 days

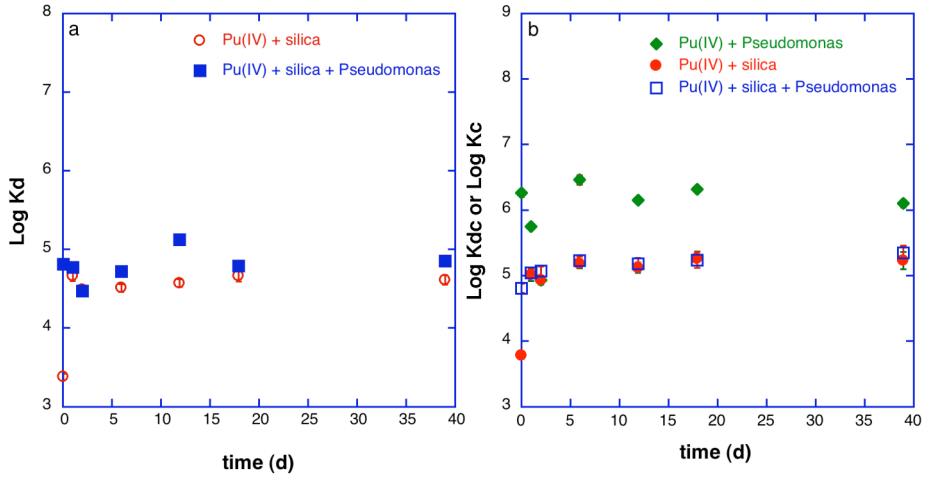

Figure 3.3. Kinetics for ternary sorption system of Pu(IV), silica particles and extracellular polymeric substance (EPS) from *Pseudomonas fluroescens* Biovar II. a) log Kd values b) log Kd_c or Kc values.

of reaction. During the 50 day experiment, a comparison of light vs. dark conditions was carried out in order to ensure that any reduction of Pu(V) as evidenced by an increase in the log Kd, could not be attributed to photreduction. The loc Kc values from EPS from *Pseudomonas fluroescens* Biovar II under light and dark conditions were nto statistically different, i.e., 5.36±0.06 and 5.48±0.05, respectively. The values of log Kd for Pu(V) and silica in the light and dark are also similar, i.e., 3.38±0.04 and 3.28±0.04 (Table 3.1). For the ternary system of silica and EPS from Pseudomonas fluorescens Biovar II, the respective light and dark values of log Kd are 3.51±0.04 and 3.45±0.04, respectively, which are again similar but substantially higher than for the binary system. Clearly there is no indication that room lighting caused photoreduction of Pu(V). The increase in

log Kc, Kd or Kd_c values over time can thus be attributed to the chemical reduction of Pu(V) by the organic material added to the experimental system.

Figure 3.2 further illustrates the role that EPS plays in regulating Pu redox status coupled to sorption. Pu(IV) equilibrated with EPS from *Pseudomonas fluorescens* Biovar II alone over 20 days had a colloidal association (83%) that is similar to that of Pu(IV), likely through the reduction of Pu(IV) followed by complexation to EPS. In addition, even though Pu(V) sorbs less strongly to silica particles than does Pu(IV), there is a significant enhancement throughout the observatin period of the log Kd in the presence of *Pseudomonas fluorescens* Biovar II EPS, over that of sorption to silica, alone. However, even after 50 days of equilibartion, log Kd values of Pu(V) steadily increase, but do not yet reach those of Pu(IV), but leaves open the possibility.

Data from several experiments with Pu(IV, V), silica and humic acid suggest that Pu strongly associates with humic acid in the colloidal (1kDa-0.45μm) fraction, likely as Pu(IV); such an association has been reported for runoff form surface soils and pond discharges (Santschi et al., 2002). In one experiment, we reversed the sequence of sorption and followed it by desorption from the particles or colloids (Tables 3.2 and 3.3). When Pu(IV) was added to humic acid first, then the mixture was equilibrated with SiO_2 particles, the experiment yielded a log Kd value that was one order of magnitude lower (2.96±0.07) than for the case when Pu(IV) was added to silica particles first (log Kd=4.23±0.11) (Table 3.2). Yet, the desorptin values of log Kd were very similar, i.e. 3.89±0.05 and 4.05±0.05. These results suggest that a fraction of the

plutonium becomes irreversibly sorbed to silica as indicated by the desorption log Kd values (when Pu is first complexed with HA) which is much higher than the sorption log Kd (Table 3.2). Yet, in the case of humic acid alone, log Kd values for sorption or desorption are statistically indistinguishable (ie., 7.10±0.12 vs. 7.17±0.10, Table 3.3), suggesting that the increase in log Kd in that case may be due to humic acids coating the silica particle, thus preventing desorption. Furthermore, if HA was added at a ten times higher concentration relative to Pu(IV) that was pre-adsorbed to SiO_2 particles, the log Kd value is lowered by about an order of magnitude (i.e., from log Kd of 4.23 at 0.5mg HA/L, Table 3.1, to log Kd of 3.26 at 5mg HA/L, Table 3.3).

Table 3.2
Particle-water partitioning coefficients of Pu(IV) to silica, log Kd (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp)) for a 2 day sorption followed by 16 days of desorption in which the sequence in which the reagents were added was reversed. Both sorption and desorption experiments were conducted in 0.1M NaClO4/50mM Tris/25mM HCl +0.5mg/L humic acid (HA).

	Sorption				Desorption			
Treatment	Log Kd	±	Log Kd_c	±	Log Kd	±	Log Kd_c	±
Pu(IV)+Si+HA	4.23	0.11	5.61	0.11	4.05	0.05	5.24	0.08
Pu(IV)+HA+Si	2.96	0.07	5.26	0.08	3.89	0.05	4.99	0.09

In a test for the solubilizing effects of humic acid, in which it acts as a surfactant, the sequence in which the reagents were added was reversed (at 0.5 mg HA/L, Table 3.2, and 5mg HA/L, Table 3.4). When plutonium was added to HA first, the log Kd was 2.79±0.04 (Table 3.5); compare this to Pu(IV) equilibration with silica first, which resulted in a log Kd of 4.59± 0.06 (Table 3.4),

i.e., almost two orders of magnitude different. However, when values of log Kd_c (which include the colloidal fraction with the particulate) are compared for the two reaction orders, the results are statistically indistinguishable: 5.48±0.12 for the case when Pu(IV) was added to HA first, and 5.68±0.08 when Pu(IV) was added to silica first (Table 3.4).

Table 3.3
Values for particle-water partition coefficients (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc = fc/(fd*Cp)) for 2 day sorption of plutonium (IV) to silica, followed by 16 day desorption in 0.1M $NaClO_4$ /50mM Tris/25mM HCl with a silica concentration of 0.5g/L and a humic acid (HA) concentration of 5mg/L.

Treatment	Log Kd	±	Log Kd_c	±	Log Kc	±
Sorption						
Pu(IV)+Si	4.58	0.08	5.61	0.08		
Pu(IV)+HA					7.10	0.12
Pu(IV)+Si+HA-particulate	3.26	0.04	5.46	0.12		
Pu(IV)+Si+HA-retentate						
Desorption						
Pu(IV)+Si	4.15	0.06	6.59	0.03		
Pu(IV)+HA					7.17	0.11
Pu(IV)+Si+HA-particulate	4.44	0.11	6.12	0.3		
Pu(IV)+Si+HA-retentate					4.13	0.08

The effect of the reaction order in which the components of the ternary system were added was also tested for the EPS from *Pseudomonas fluorescens* Biovar II, with similar results (Table 3.4). The change was slightly less dramatic, partly because the log Kd when equilibrated with EPS first was much higher than that when equilibrated to humic acid first (3.76 ± 0.06 vs. 2.79 ± 0.04, Table 3.4), demonstrating the higher (SiO_2) surface activity of Pu(IV) complexed to EPS (as opposed to HA). The log Kd values for the case when Pu was added to silica first were much closer, regardless of which organic colloid was added, i.e., 4.74 ±

0.07 when EPS was added after the silica, vs. 4.59 ± 0.06 for the case when HA was added after the silica.

Table 3.4
Test of reversal of reaction order: Sorption of Pu(IV) equilibrated with the first listed component for 2 hours followed by a 2 day equilibration for the ternary system in 0.1M $NaClO_4$/ 50mM Tris/ 25mM HCl, with a silica (Si) concentration of 0.5g/L, and humic acid (HA) or EPS concentration of 5mg/L. (Kd = fp/((fc+fd)* Cp), Kd_c = (fp+fc)/(fd*Cp)).

	Log Kd	±	Log Kd_c	±
Pu(IV)+Si+HA	4.59	0.06	5.68	0.08
Pu(IV)+HA+Si	2.79	0.04	5.48	0.12
Pu(IV)+Si+EPS	4.74	0.07	5.11	0.09
Pu(IV)+EPS+Si	3.76	0.06	5.02	0.11

Table 3.5
Log Kd values (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp)) for Pu(V) to silica in the presence of different organic colloids to test for the ability to reduce (V) to (IV), after 2 days of equilibration. Effective reduction would be indicated by higher log Kd values closer to those of Pu(IV) (log Kd = 4.5-5.5).

	Log Kd	±	Log Kd_c	±	Mass Balance(%)
Pu(V)+Si	2.41	0.07	2.74	0.05	61 ± 4
Pu(V)+Si+HA	2.38	0.05	3.65	0.05	60 ± 3
Pu(V)+Si+EPS	2.59	0.15	2.74	0.15	45 ± 6
Pu(V)+Si	2.77	0.06	3.12	0.06	67 ± 7
Pu(V)+Si+HQ	3.11	0.05	3.98	0.05	95 ± 9
Pu(IV)+Si+glu	2.61	0.06	2.91	0.05	87 ± 8

Finally, the ability of compounds such as EPS from different bacteria (and phytoplankton) cultures and commercially available organic compounds e.g. humic acid, hydroquinone and glucose, were tested for their ability to reduce Pu(V) to Pu(IV) during a ternary adsorption experiment. Oxidation states could not be measured directly as this would have been nearly impossible given the

low concentrations used, and the tendency of humic acid associated Pu(IV) to collect at the interface during solvent extractions (Santschi et al., 2002). Instead, Log Kd values of Pu(V) were compared to Pu(IV), with the assumption that the closer the log Kd for Pu(V) approached that of Pu(IV) (~4.5), the more reduction from (V) to (IV) had occurred. Although, all the organic compounds that were tested should have the ability to reduce Pu(V) to Pu(IV), hydroquinone was the only one, after equilibration of 2 days, to show an increase in the log Kd of plutonium (V) in the ternary system over the log Kd to silica alone (Table 3.5). When EPS from five different bacteria and phytoplankton cultures were equilibrated for 2 days with Pu(V) and silica particles (Table 3.6), there was little evidence of an increase in the log Kd that would suggest that any of the EPS samples would be able to reduce the Pu(V) to Pu(IV), thereby rendering Pu more particle reactive over that time scale. However, over longer time scales, there was a slow but steady increase in Kd for all organic compounds employed (see below). Furthermore, as in the case of the model organic compounds, there seems to be a significant (33% for all EPS) association of the Pu(V) with the colloidal organic macromolecule (i.e., EPS) fraction, which is not the case for the pure Pu(V) tracer, where the colloidal fraction was only about 3% (see methods section), contrary to that of Pu(IV), where this fraction was more than an order of magnitude larger (Figure 3.1). Pu(V) itself has only a weak sorption and/or complexation ability. A longer-term sorption experiment that lasted 50 days (Figure 3.2) confirmed that the main difference between the different organic compounds lay in their reduction kinetics. EPS from *Pseudomonas fluorescens*

Biovar II consistently enhanced the Kd of Pu(V) to silica particles, which itself increased throughout the experiment (Figure 3.2a). This enhancement effect of EPS is, however, not seen in the values of Kd_c, which increased similarly to those of Kd. After about 20 days, values of log Kc of Pu(V) to EPS from *Pseudomonas fluorescens* Biovar II (Figure 3.2b) became undistinguishable from those of Pu(IV) (Figure 3.3b). Thus, our data suggest that Pu(V) is reduced to Pu(IV) that is associated with a more soluble (i.e., more hydrophilic) colloidal organic fraction, as plutonium in the colloidal phase was greatly enhanced by all of the organic compounds tested. Log Kd values of Pu(IV) to silica remained rather constant from 2 to 50 days (Figure 3.3a), but were enhanced to the same extent by the presence of EPS from *Pseudomonas fluorescens* Biovar II, as in the case of Pu(V). Log Kd_c values, on the other hand, did not show this enhancement effect (Figure 3.3b), suggesting that the partitioning between particulate and colloidal Pu, one one hand, to low molecular Pu, shows similarities between Pu(IV) and Pu(V).

Table 3.6
Sorption of Pu(V) to silica in the presence or absence of EPS from different bacteria and phytoplankton species.(Kd = fp/((fc+fd)*Cp), Kd_c=(fp+fc)/(fd*Cp), Kc=fc/(fd*Cp)). For comparison Pu(V) to silica alone gave a log Kd of 2.41±0.07.

Treatment	Time (day)	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total)
Pu(V)+*Synecococcus*	4					4.86	0.10	88 ± 7
Pu(V)+Si+ *Synecococcus*	4	2.30	0.10	2.95	0.10			72 ± 7
Pu(V)+*E. huxleyi*	4					4.28	0.11	106 ± 8
Pu(V)+Si+ *E. huxleyi*	4	2.36	0.04	2.51	0.05			97 ± 6
Pu(V)+ *Skeletonema*	4					4.49	0.11	100 ± 8
Pu(V)+Si+ *Skeletonema*	4	2.57	0.06	2.92	0.06			111 ± 8
Pu(V)+*S. stellata*	4					4.93	0.09	66 ± 6
Pu(V)+Si+ *S. stellata*	4	2.55	0.05	2.87	0.05			100 ± 5
Pu(V)+*Pseudomonas*	4					5.09	0.07	97 ± 6
Pu(V)+Si+ *Pseudomonas*	4	2.88	0.06	3.32	0.07			81 ± 6

3.5 Conclusions

Investigation of Pu(V) kinetics of particle-water partitioning in the presence or absence of natural organic matter compounds indicates that Pu(V) requires quite a long time (>50 days) to reach a quasi-equilibrium state. Comparison of sorption under normal room light and dark conditions after 50 days showed no significant contribution of photoreduction. Log Kd values of Pu(V) to silica particles steadily increased (by a factor of 30) over the observation period of 50 days (regardless of light), likely indicating reduction due to the presence of colloids. Furthermore, Pu(V) sorption to silica particles and EPS from *Pseudomonas fluorescens* Biovar II was significantly and consistently enhanced over that of silica alone.

A test of the reaction order, i.e., the sequence in which organic compounds (humic acid or EPS) or silica particles were added, showed a significant enhancement in the resulting log Kd values when Pu(IV) was added to silica particles first. The resulting log Kd was always lower when humic acid or EPS were added before the silica particles, indicating that sorption reactions to silica can be, at least in part, irreversible. The redox potentials reported in the literature indicate that model organic compounds such as humic acid, hydroquione and glucose should reduce Pu(V) to Pu(IV). However, even though hydroquinone showed some enhancement in colloidal Pu after 2 days, EPS isolated from several bacterial and phytoplankton species showed no significant increase in the log Kd after 2 days of equilibration, yet seemed to strongly associate with the colloidal fraction. However, after 20 days of equilibration with EPS from *Pseudomonas fluorescens* Biovar II, log K_c values for Pu(V) were indistinguishable from those of Pu(IV), suggesting slow reduction of Pu(V) to Pu(IV) followed by complexation to a less surface active fraction of EPS. It thus appears that regardless of the organic fraction, all of them have the capability for Pu(V) reduction, albeit at different rates. However, the organic colloids that were tested (e.g., EPS, etc.) appear to consist of different fractions with different complexation capacity and surface activity (i.e., amphiphilicity), which can lead to enhancements of Kd values for both Pu(V) and Pu(IV) for some EPS, e.g., from EPS from *Pseudomonas fluorescens* Biovar II.

4. PARTICLE-WATER PARTITION COEFFICIENTS FOR SEDIMENT TRAP MATERIAL: A COMPARISON OF GULF OF MEXICO TO ARCHIVED TIME SERIES (BATS AND HOT) SAMPLES

4.1 Overview

Particle-water partition coefficients (Kd) for radionuclides of thorium, protactinium and plutonium were calculated for sediment trap material collected in 2006 from the Gulf of Mexico (GOM) from the upper 140m. Particle-water partition coefficients in these newly acquired samples were compared with those determined with archived sediment trap material from time series stations (BATS in the Atlantic near Bermuda and HOT in the Pacific near Hawaii). Samples were not directly comparable due to differences in storage times and depths, i.e., GOM samples from the euphotic zone (<140m), samples from the BATS station, taken from the "twilight zone" (500-3200m), and samples from the HOT station taken from deep Pacific waters at 4000m. Results showed a highly signficant and positive correlation between Log Kd of thorium (and protactinium) with the calcium carbonate content. Yet, extrapolating to 100 % $CaCO_3$ would suggest log Kd values that would be 3 orders of magnitude higher than determined in laboratory experiments and available from the literature. Thus, other co-occurring phases, such as carbohydrate-rich exopolymeric substances (EPS) could be responsible for binding the actinides. As a matter of fact, a significant positive correlation between the contents of total carbohydrates and calcium carbonate that is evident from the results of the BATS samples, thus confirming this hypothesis.

4.2 Introduction

Thorium and protactinium have long been used as tracers of oceanic processes. In particular, the ratio of the two longer-lived ^{231}Pa and ^{230}Th, have been used to assess boundary scavenging, ocean circulation, and paleoproductivity. However, thorium to protactinium ratios in suspended or sinking particles can vary as a function of depth and size (Walter et al. 2001). There are several theories as to what causes the fractionation between these two isotopes. It may be a result of Pa(V) being reduced to the more particle reactive Pa(IV). Others believe there that the cause of Th/Pa fractionation lies in the type of inorganic sorbents that exhibit different affinities to Pa or Th. For example, Luo and Ku (1999) propose that the changing Th/Pa ratios are due to changing biogenic opal to clay ratios, while Chase et al., 2002 believe that Th/Pa fractionation is due to changing opal to carbonate ratios. However, laboratory experiments demonstrate that the log Kd values of Th and Pa on different types of inorganic particles can be different from those observed in the oceanic environment. Work by our group has investigated the importance of different types of macromolecular organic matter on the sorption of actinides onto organic or inorganic particles and have come to the conclusion that it is not only the presence of organic moieties that control the extent of adsorption onto particles, but especially the type of organic matter. For example laboratory experiments with varying types of organic matter showed that the closest log Kd

value to that found in the aquatic environment was from natural polysaccharidic organic material (Quigley et al., 2002).

Plutonium is not as widely used as an oceanic tracer as the Th/Pa pair. However, its fate in the environment is also dependent on its interactions with particles. Like Pa, Pu can occur in the environment in different oxidation states, with (IV) being the most particle-reactive, but (V) likely being the dominant form in the oceans (Choppin & Wong, 1998). The use of Pu tracer in both the (IV) and (V) oxidation states should give some insight as to the effect of redox state of Pu sorption to determine what effect if any this may have on the fractionation. Because of this, and the laboratory nature of this study, Pu will be included in this study.

To address the issue of what causes fractionation between thorium and protactinium, this study will utilize log Kd values determined from tracer experiments performed onboard on freshly collected sediment trap material, archived sediment trap material from different oceans and different depths, and review of data in the literature.

4.3 Methods

4.3.1 Gulf of Mexico (GOM)

In May 2006, surface sediment traps (<150m) were deployed at three stations (Station 1 located at 25° 52.308'N, 92° 31.098'W, Station 2 located at 26° 54.588'N, 89° 59.448'W and Station 3 located at 27° 52.11'N, 88° 38.448'W) in the Gulf of Mexico for a 48 hour period before recovery aboard the R/V Seward

Johnson. Once recovered, plastic tubes were allowed to settle before the surface water was drained by untaping drain holes higher up in the tube. The remaining material was transferred to a 1L bottle and homogenized prior to distribution to different users.

For the log Kd experiments, 50mL of sediment trap slurry was pipetted into a 50mL centrifuge tube along with Tris/HCl solution for a final concentration of 20mMTris/10mMHCl, to maintain pH of the system even after adding tracers. To each tube the appropriate tracer, ^{233}Pa added in equilibrium with ^{237}Np, ^{234}Th, or ^{240}Pu was added. The tube was mixed and the pH measured. The tubes were then placed on the lab bench in a spill tray, which, with the natural rolling of the research boat, acted as a roll tray to mix the samples. The tubes were mixed for 48 hours after which time the pH was measured (i.e., 7.4 to 8.1), and the samples were then fractionated. Size fractionation was carried out first by filtration onto pre-weighed filters for calculation of particle concentration. 0.4um filters were typically used but in the case of ^{234}Th other sizes 50um, 10um and 1um filters were also used for comparison of log Kd values among size classes used for our larger scale in-situ ^{234}Th size fractionation measurement. In selected cases, the filtrate was ultrafiltered using a 1kDa ultrafilter in a stirred cell ultrafiltration apparatus. Ultrafiltration separated what passed through the 0.4μm filter into 1kDa – 0.4 and <1kDa fractions. ^{234}Th and ^{233}Pa activities were determined by gamma counting on a well germanium counter at 63keV and 312 keV respectively. To the plutonium samples, known amount of ^{242}Pu tracer was added and the

samples processed through ion exchange columns followed by lanthanum fluoride precipitation and alpha counting (Joshi, 1985).

4.3.2 Bermuda Atlantic Time Series (BATS)

Archived sediment trap material (<125μm in size), from BATS OFP station, located 31° 50′ N, 64° 10′ W, collected at depths of 500m, 1500m, and 3200m, was received from Dr. Maureen Conte, Bermuda Biological Station for Research. Aliquots of this freeze-dried material were resuspended in pre-ultrafiltered seawater (<1kDa), to which Tris/HCl was added to replicate conditions used in the shipboard experiments. 2mg/L concentration of this material was used as that represented an average of what was found in the Gulf of Mexico sediment traps. ^{233}Pa, added in equilibrium with ^{237}Np, and ^{234}Th tracers, were added to each tube. The suspension was shaken, this time on a shaker table in the lab, for 2 days with the pH being checked before and after to watch for pH drift (i.e., pH of 7.8 to 8.2). Size fractionation and gamma counting followed as previously described.

4.3.3 Hawaii Oceanic Time Series (HOT)

Sediment trap samples from HOT Aloha station (22° 45′N, 158° 00′W) were provided by Dr. Dave Karl, Dept. of Oceanography, University of Hawaii, as a frozen slurry of filtered seawater, with a final concentration of 1% formaldehyde and 5g/L NaCl. These samples had been previously thawed for characterization in our laboratory and were likely stored in the refrigerator in excess of 1.5 years prior to partitioning experiments. From the slurry, 50ml was pipetted to a centrifuge tube to which ^{233}Pa, in equilibrium with ^{237}Np, and ^{234}Th

tracers were added. Tris/HCl solution was also added to maintain neutral pH, yet given the preservation state of this material, five times the amount of buffer was used and yet, the pH was still below neutral (5.5 – 6). HOT samples were filtered on to pre-weighed 0.4μm filters that were subsequently dried and weighed for a minimum of 3 times, in order to calculate an average particulate concentration.

4.3.4 Particle-water partition coefficient

The particle-water partitioning values (log Kd and log Kd_c) were calculated two ways.

Particulate = silica: $Kd = fp/((fc+fd)*Cp)$

Particulate = silica + retentate: $Kd_c = (fp+fc)/(fd*Cp)$

Where fp = fraction on the particles; fc = fraction retained by 1kDa ultrafilter (retentate); fd = fraction that passes through a 1kDa ultrafilter (permeate); Cp is the particle concentration (g/mL); Kd = particle-water partitioning coefficient (traditional); Kd_c = particle-water partitioning coefficient including the retentate in the particulate.

4.4 Results

4.4.1 Gulf of Mexico (GOM)

The size fraction comparison (50μm, 10μm, 1μm and 0.4μm) could not be completed for the Gulf of Mexico samples, as the concentration of particles for the larger size fractions 50μm, 10μm, and 1μm were too low to be measured on

the analytical balance. Thus, all results given here are for the 0.4μm filtered samples only.

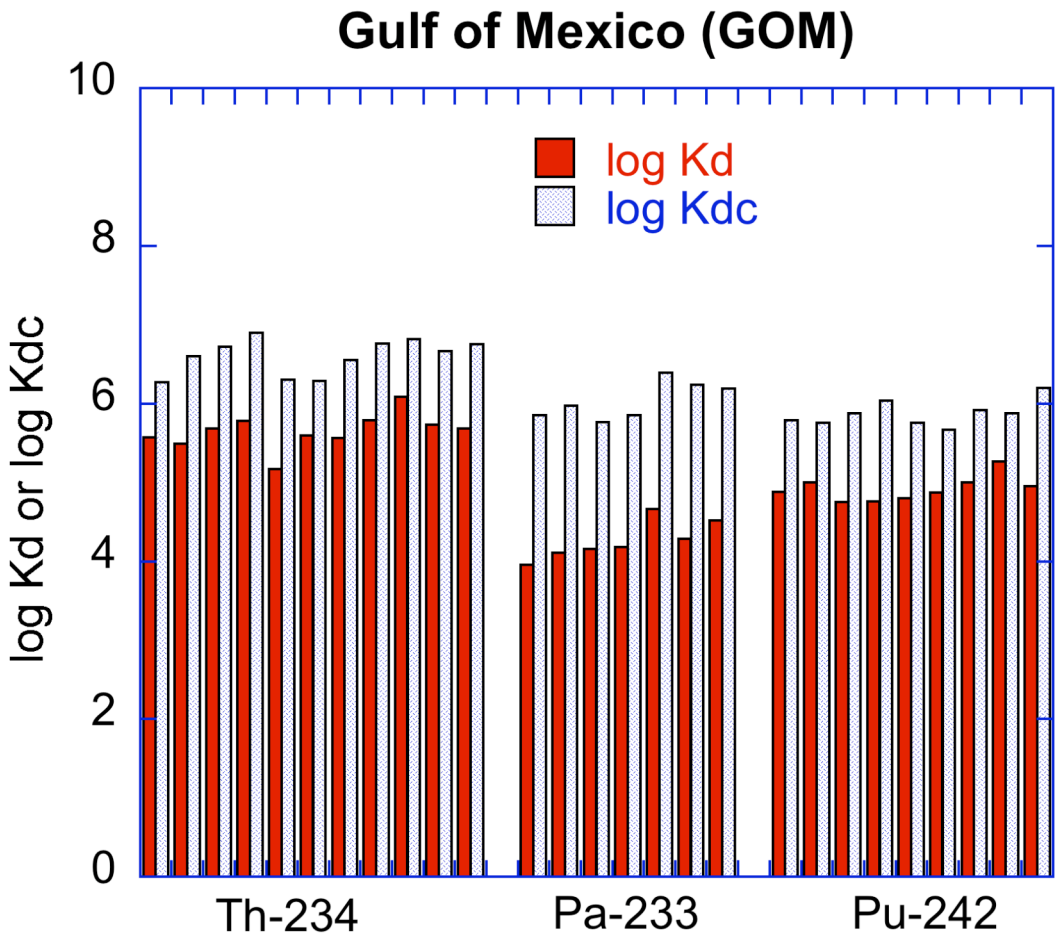

Figure 4.1. Log Kd and log Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu for sediment trap material collected in the Gulf of Mexico in May, 2006. (log Kd = fp/((fc+fd)*Cp) and log Kd_c =(fp+fc)/(fd*Cp))

Log Kd and log Kd_c values for ^{234}Th, ^{233}Pa, and ^{240}Pu, including one case of Pu(V) are found in Tables 4.1 and 4.2. A comparison of the log Kd and Log Kd_c values (Figure 4.1), clearly shows that for the GOM samples, the log Kd_c value is always significantly higher than that of log Kd. Such data indicates that all three radioisotopes are associated with a colloidal fraction that is not associated

with the particles. Depth profiles for all three isotopes for Stations 1, 2, and 3 are found in Figures 4.2, 4.3, and 4.4 respectively. Again, a disparity between the log Kd and log Kd_c values is seen, with no clear depth dependence. Stations 1 and 3 were located in a cold core ring, and Station 2 in a warm core ring, yet no significant trends are evident in the depth profiles.

Table 4.1
Particle-water partitioning data (log Kd) for sediment trap material collected in the Gulf of Mexico in May 2006 for ^{234}Th, ^{233}Pa (added in equilibrium with ^{237}Np) where Kd = fp/((fc+fd)*Cp), and Kd_c = (fp+fc)/(fd*Cp).

Station	Depth	^{234}Th Log Kd	±	^{234}Th Log Kd_c	±	^{233}Pa Log Kd	±	^{233}Pa Log Kd_c	±
S1	65m	5.57	0.02						
		5.57	0.01	6.27	0.02				
	90m	5.49	0.01	6.6	0.02				
	120m	5.68	0.02						
		5.84	0.01	6.72	0.01				
	140m	5.78	0.01	6.9	0.02	4.24	0.07		
S2	65m	5.17	0.02						
		5.28	0.01	6.3	0.01	3.96	0.06	5.85	0.06
	90m	5.6	0.02						
		5.39	0.01	6.29	0.01	4.11	0.07	5.97	0.07
	120m	5.56	0.02						
		5.78	0.01	6.55	0.01	4.16	0.06	5.77	0.07
	140m	5.79	0.01	6.76	0.02				
						4.18	0.07	5.85	0.07
S3	65m	5.97	0.02						
		6.09	0.01	6.82	0.02	4.66	0.06	6.39	0.07
	90m	5.63	0.02						
		5.73	0.01	6.67	0.02	4.29	0.06	6.24	0.08
	120m	5.48	0.02						
		5.68	0.01	6.75	0.01	4.51	0.06	6.19	0.07
	140m	5.62	0.02						

Table 4.2
Particle-water partitioning data (log Kd) for sediment trap material collected in the Gulf of Mexico in May 2006 for ^{240}Pu. (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp))

Station	Depth	^{240}Pu Log Kd	±	^{240}Pu Log Kd_c	±	^{240}Pu (V) Log Kd	±	^{240}Pu (V) Log Kd_c	±
S1	65m	4.88	0.03	5.79	0.03				
	120m	5	0.03	5.76	0.02				
	140m	4.75	0.02	5.88	0.02				
S2	65m	4.76	0.05	6.04	0.03				
	90m	4.8	0.04	5.76	0.05				
	120m	4.87	0.04	5.67	0.04	3.58	0.08	5.61	0.03
	140m	5	0.04	5.92	0.04				
S3	65m	5.27	0.03	5.88	0.03				
	90m	4.95	0.03	6.2	0.02				

A comparison of Pu(IV) to Pu(V) was successfully conducted in one of the samples, Station 2 - 120m. As also observed in Section 3, there is a marked difference between the log Kd values (4.87 ± 0.04 for Pu(IV) and 3.58 ± 0.08 for Pu(V)) but no difference between the log Kd_c values (5.67 ± 0.04 and 5.61 ± 0.03, respectively) is seen here. Convergence of the log Kd_c values from such different log Kd values indicates a reduction of Pu(V) by the colloidal matter, likely organic in nature, and strong association with both Pu oxidation states to the colloidal fraction which does not have an association with the particulate

fraction. This confirms the findings in the lab experiments conducted in Section 3.

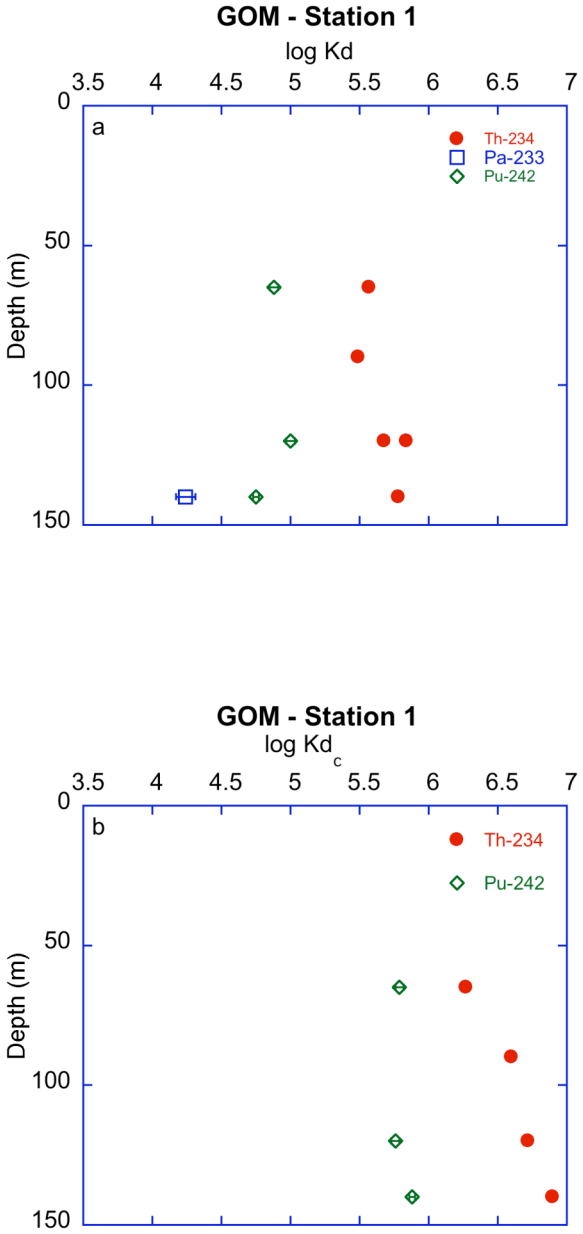

Figure 4.2. Depth profiles for ^{234}Th, ^{233}Pa, and ^{240}Pu at Station 1 in the Gulf of Mexico, May 2006 for a) log Kd and b) log Kd_c.

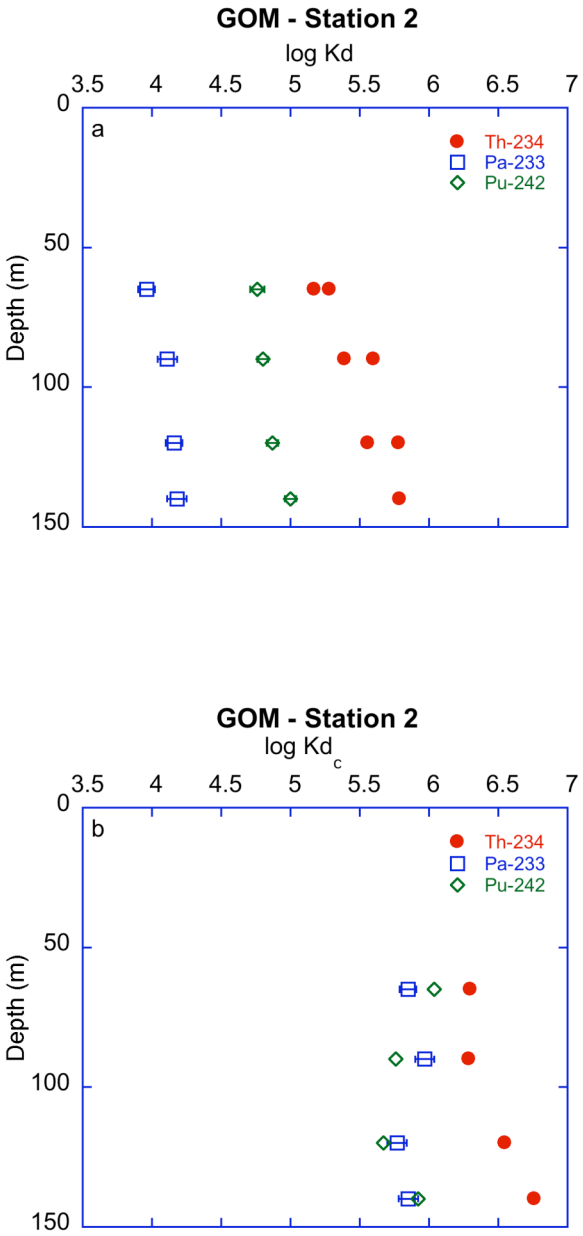

Figure 4.3. Depth profiles for ^{234}Th, ^{233}Pa, and ^{240}Pu at Station 2 in the Gulf of Mexico, May 2006 for a) log Kd and b) log Kd_c.

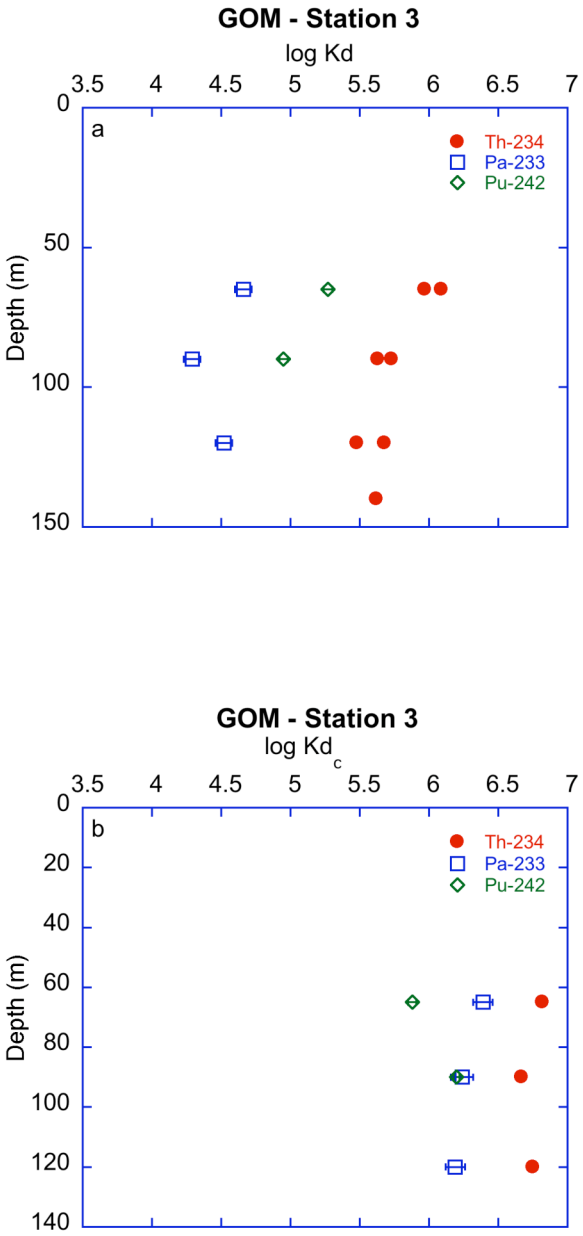

Figure 4.4. Depth profiles for ^{234}Th, ^{233}Pa, and ^{240}Pu at Station 3 in the Gulf of Mexico, May 2006 a) log Kd and b) log Kd_c.

4.4.2 Bermuda Atlantic Time Series (BATS)

Table 4.3
Particle-water partitioning data (log Kd) for freeze-dried sediment trap material collected at the Bermuda Atlantic Time Series station (BATS) resuspended in <1kDa seawater with Tris/HCl added for ^{234}Th, where Kd = fp/((fc+fd)*Cp), and Kd_c = (fp+fc)/(fd*Cp).

ID	Depth (m)	Date	Th-Log Kd	±	Th-Log Kd_c	±
9/00-3	500	6/20/00	6.68	0.08	6.97	0.12
9/00-3	1500		6.27	0.08	6.35	0.09
9/00-3	3200		6.73	0.08	6.77	0.09
1/01-1	500	9/29/00	4.62	0.07	5.82	0.10
1/01-2	500	10/4/00	5.71	0.05	6.04	0.07
5/01-1	500	1/19/01	6.42	0.10	7.18	0.38
5/01-1	1500		6.52	0.11	7.48	0.71
5/01-1	3200		6.60	0.12	7.64	1.49
5/01-4	500	3/7/01	6.86	0.18	6.88	0.20
5/01-4	1500		6.77	0.11	7.15	0.20
5/01-4	3200		6.92	0.17	7.28	0.38
9/01-1	500	5/11/01	6.35	0.08	6.80	0.18
9/01-1	1500		5.96	0.07	6.07	0.09
9/01-1	3200		6.44	0.14	6.96	0.35
9/01-8	500	8/27/01	6.1	0.06	6.12	0.07

Thorium and protactinium log Kd and Log Kd_c values for BATS samples are found in Tables 4.3 & 4.4. A comparison of the two shown by isotope (Figure 4.5), demonstrates that for most samples, as seen in the case of Gulf of Mexico samples, the log Kd_c is higher than the log Kd. These samples are from depths of 500m, 1500m, and 3200m, which are much deeper than the Gulf of Mexico samples that were taken from 140m or less. Yet, the disparity between the log Kd and log Kd_c values still indicates association of thorium and

protactinium with a colloidal phase that is not associated with the particles and has not been degraded as a result of depth in the water column nor storage for almost 7 years as freeze-dried material. BATS samples, plotted against time to look for seasonal variation, showed no major differences (Figure 4.6). Depth profiles in Figures 4.7a and 4.7b showed no significant trends with depth for either thorium or protactinium.

Table 4.4
Particle-water partitioning data (log Kd) for freeze-dried sediment trap material collected at the Bermuda Atlantic Time Series station (BATS), resuspended in <1kDa seawater with Tris/HCl added ^{233}Pa (added in equilibrium with ^{237}Np), where Kd = fp/((fc+fd)*Cp), and Kd_c = (fp+fc)/(fd*Cp).

ID	Depth (m)	Date	Pa-Log Kd	±	Pa-Log Kd_c	±
9/00-3	500	6/20/00	6.87	0.08	8.47	0.04
9/00-3	1500		6.41	0.06	8.14	0.04
9/00-3	3200		6.91	0.05	7.91	0.03
1/01-1	500	9/29/00	3.90	0.07	5.52	0.06
1/01-2	500	10/4/00	5.83	0.09	8.07	0.07
5/01-1	500	1/19/01	5.69	0.05	8.19	0.04
5/01-1	1500		6.06	0.04	8.33	0.04
5/01-1	3200		6.12	0.04	8.46	0.04
5/01-4	500	3/7/01	6.54	0.07	8.26	0.04
5/01-4	1500		6.06	0.04	8.82	0.05
5/01-4	3200		6.12	0.043	8.62	0.04
9/01-1	500	5/11/01	6.19	0.05	8.02	0.04
9/01-1	1500		6.40	0.08	7.72	0.04
9/01-1	3200		6.44	0.79	8.26	0.161
9/01-8	500	8/27/01	6.49	0.07	7.91	0.07

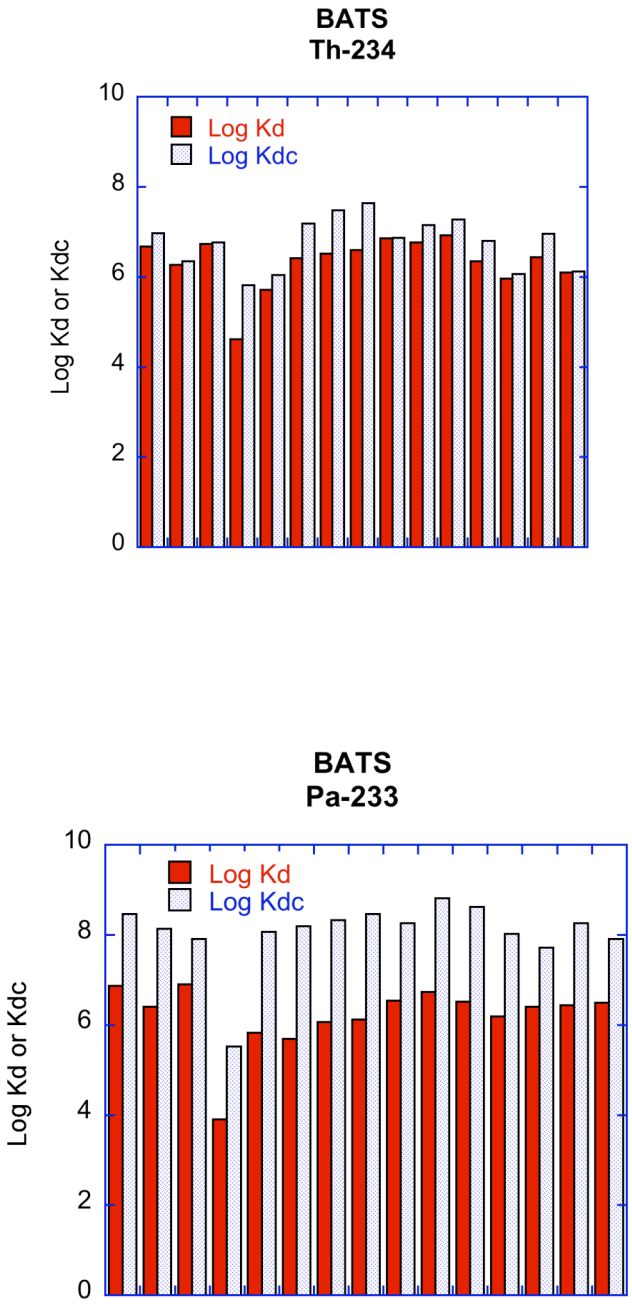

Figure 4.5. Log Kd and log Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu for sediment trap material collected at Bermuda Atlantic Time Series (BATS) in 2000-2001. (log Kd = fp/((fc+fd)*Cp) and log Kd_c =(fp+fc)/(fd*Cp))

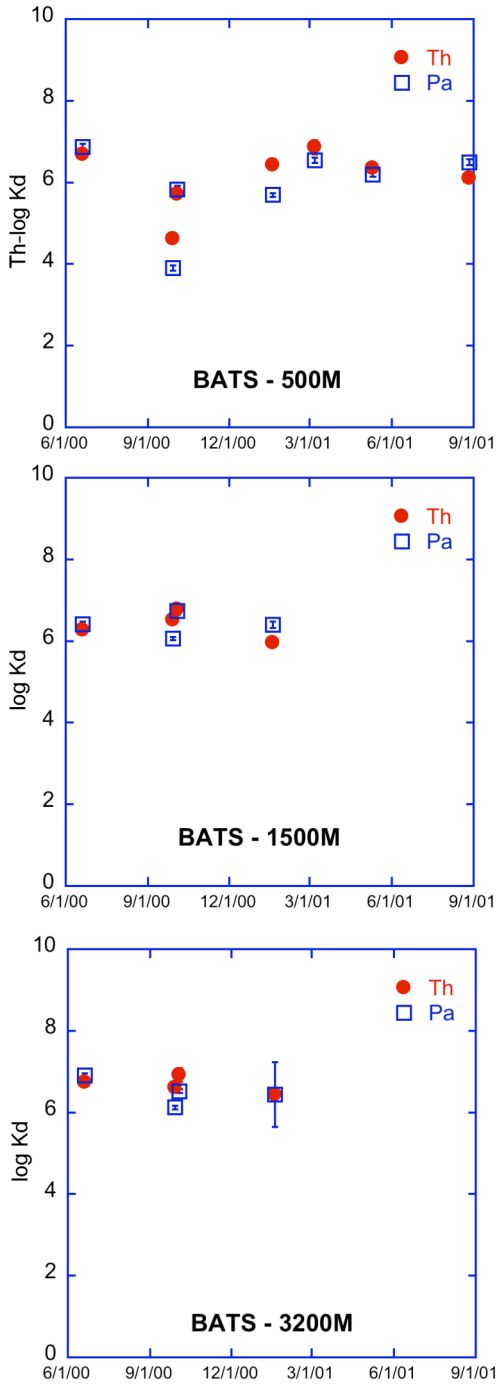

Figure 4.6. Log Kd values for BATS as a function of time.

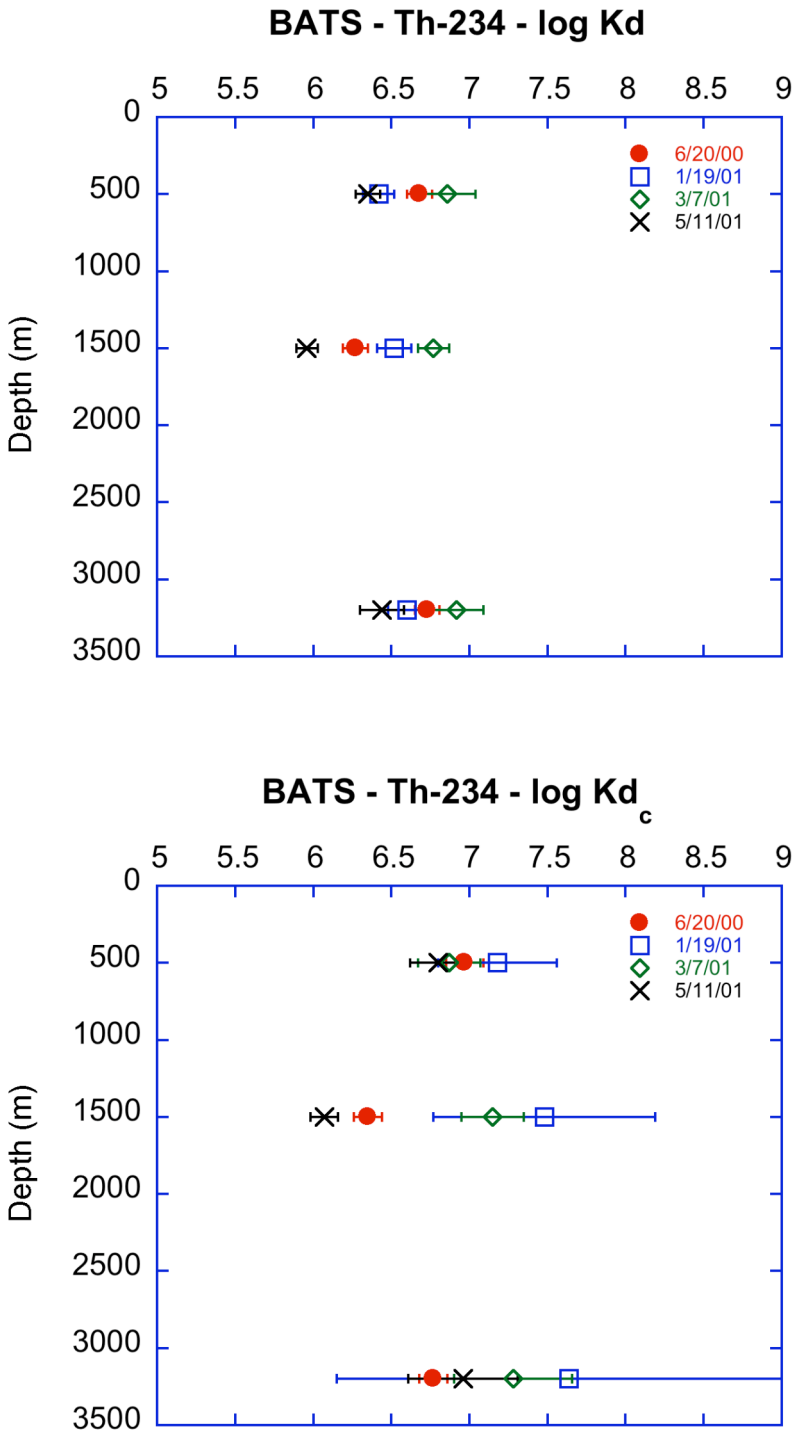

Figure 4.7a. BATS depth profiles for ^{234}Th log Kd and log Kd_c values.

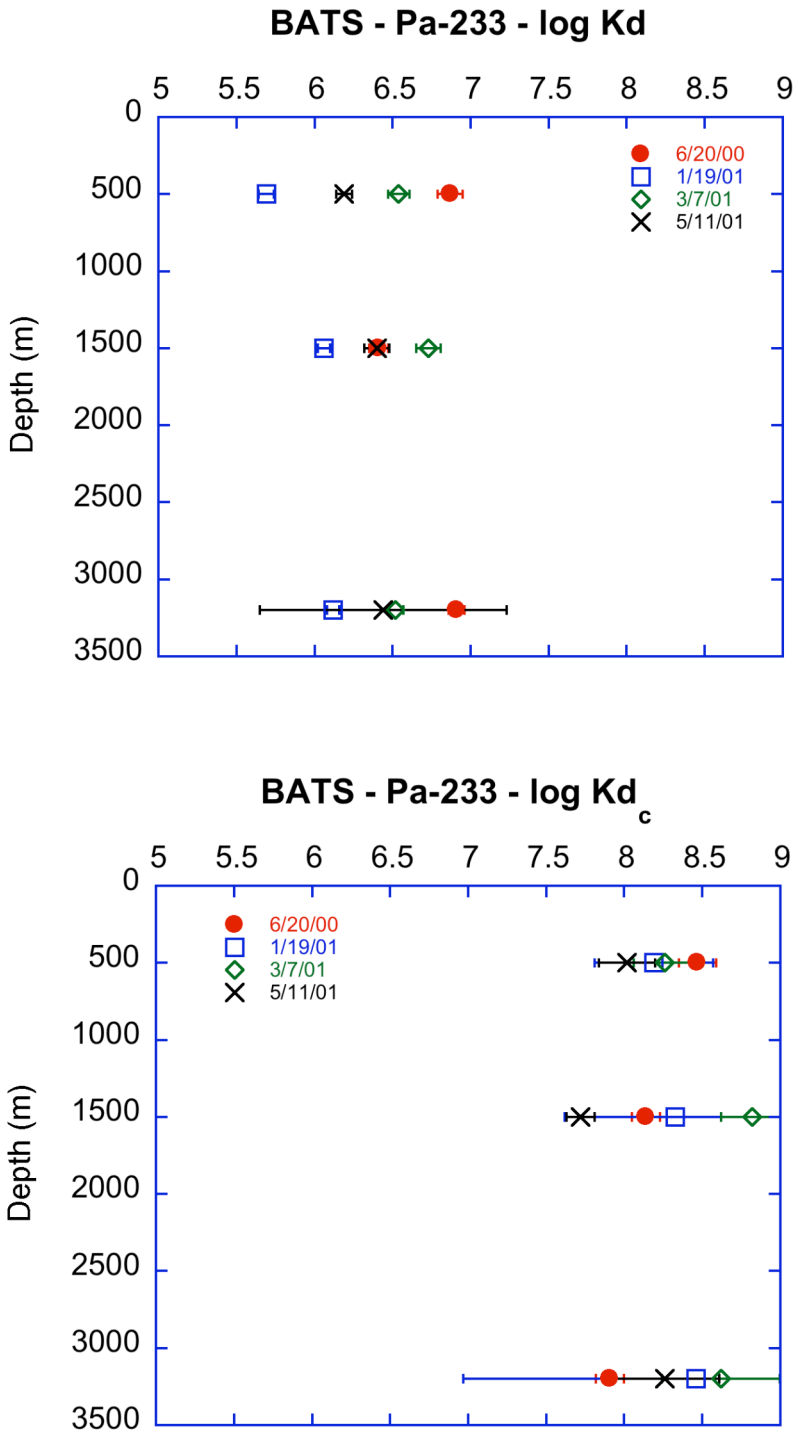

Figure 4.7b. BATS depth profiles for ^{233}Pa log Kd and log Kd_c values.

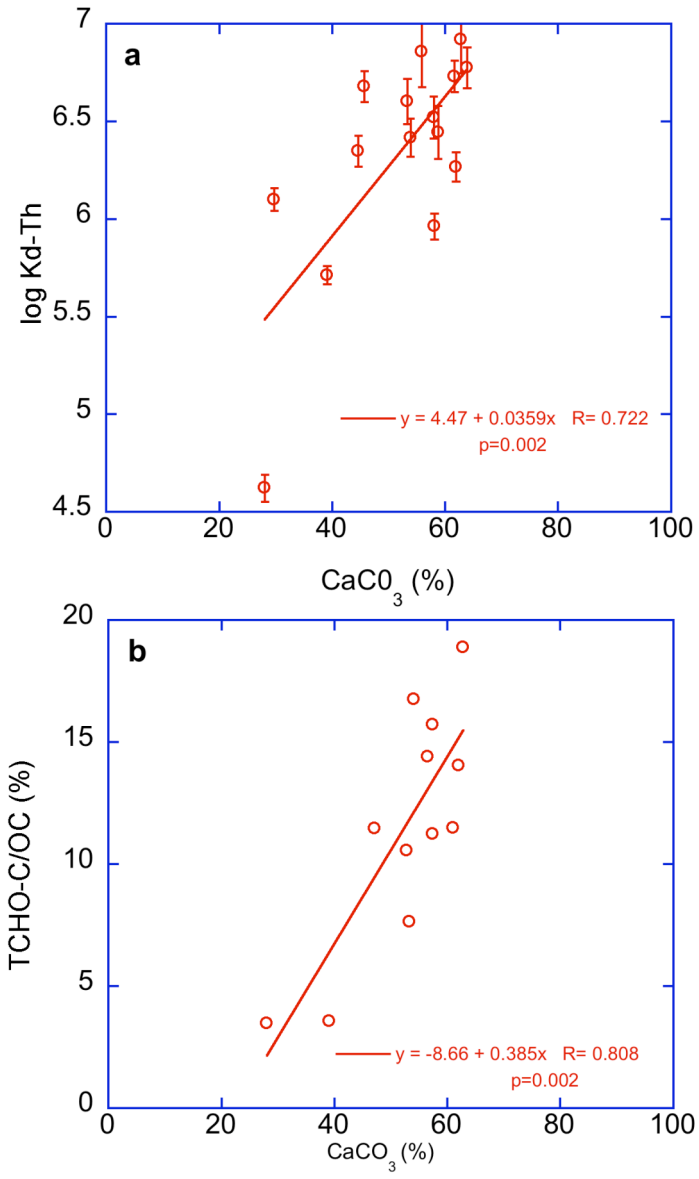

Figure 4.8. Correlations between a) log Kd for ^{234}Th and calcium carbonate and b) total carbohydrates (TCHO) (Hung, pers. comm.) and calcium carbonate content in BATS samples.

Compositional data such as % calcium carbonate, % carbon and % nitrogen were provided by Maureen Conte for the BATS samples. Correlations were attempted for thorium data and these three constituents. A positive correlation was seen with log Kd for thorium and the calcium carbonate of these samples (Figure 4.8a). Three components of the organic carbon fraction were analyzed in a subset of BATS samples for protein, uronic acids and total carbohydrates. All three components were also compared to calcium carbonate, of which, only the total carbohydrates showed a significant and positive correlation (Figure 4.8b).

4.4.3 Hawaii Oceanic Time Series (HOT)

Table 4.5
Particle-water partitioning data (log Kd) for formaldehyde preserved sediment trap material (4000m) from Hawaii Oceanic Time Series Station (HOT), with Tris/HCl and ^{234}Th added where Kd = fp/((fc+fd)*Cp), and Kd_c = (fp+fc)/(fd*Cp).

ID	Date	Th-Log Kd	±	Th-Log Kd_c	±
TRAP2-5-D	1/24/99	6.36	0.26	[a]	
TRAP2-6-D	2/9/99	6.99	0.48	[a]	
TRAP2-7-D	2/26/99	[a]		[a]	
TRAP2-8-D	3/14/99	[a,b]		[a,b]	
TRAP2-9-D	3/31/99	[a,b]		[a,b]	
TRAP2-10-D	4/16/99	[a]		[a]	
TRAP2-11-D	5/3/99	5.42	0.45	6.54	0.68
TRAP2-12-D	5/19/99	[a,b]		[a,b]	
TRAP2-13-D	6/5/99	6.33	0.78	6.91	0.15

[a] no measurable activity in the permeate
[b] no measurable activity in the retentate

Particle-water partitioning coefficient calculations for thorium in the Hawaii time series stations could often not be completed due to unmeasurable

activity in the permeate and sometimes in the retentate as well (Table 4.5). Although, log Kd values could not be calculated for all samples, qualitatively one can see that these values would be higher than those reported for the other samples in that all of the measurable thorium is associated with the particles. Protactinium, on the other hand, was measurable for these samples and log Kd and log Kd_c are reported in Table 4.6. HOT samples are the only of the three sets analyzed here to show no difference between log Kd and log Kd_c values (Tables 4.5 & 4.6, Figure 4.9). Although thorium data is limited, no trend over time is seen in either the thorium or protactinium log Kd (Figure 4.10). It is unclear from this data set whether this is a function of depth as these are the deepest (4000m) samples in this study or whether lack of colloidal association is a result of preservation methods. These samples are also the oldest. The sediment-water slurry was preserved with formaldehyde to which 5g/L NaCl was added and then frozen. Characterization of these samples was conducted in this lab a year and a half prior to these experiments during which time the samples were stored thawed in a refrigerator. Another difference in these samples is the presence of formaldehyde, a reducing agent, which could reduce Pa(V) to Pa(IV) resulting in log Kd values for ^{233}Pa which are similar to ^{234}Th (log Kd ~ 6-7). Thus, the presence of formaldehyde could be responsible for maximizing sorption onto particles without a strong colloidal association as seen in the Gulf of Mexico and BATS samples, or higher salt content.

Table 4.6
Particle-water partitioning data (log Kd) formaldehyde preserved material collected at the Hawaii Oceanic Time Series Station (HOT) with Tris/HCl and ^{233}Pa (in equilibrium with ^{237}Np) added, where Kd = fp/((fc+fd)*Cp), and Kd_c = (fp+fc)/(fd*Cp).

ID	Date	Pa-Log Kd	±	Pa-Log Kd_c	±
TRAP2-5-D	1/24/99	5.97	0.01	6.18	0.01
TRAP2-6-D	2/9/99	5.71	0.01	5.83	0.01
TRAP2-7-D	2/26/99	5.90	0.01	7.24	0.51
TRAP2-8-D	3/14/99	5.79	0.01	5.81	0.01
TRAP2-9-D	3/31/99	5.61	0.01	5.65	0.01
TRAP2-10-D	4/16/99	6.15	0.01	6.33	0.01
TRAP2-11-D	5/3/99	5.44	0.01	5.87	0.01
TRAP2-12-D	5/19/99	5.94	0.03	5.99	0.01
TRAP2-13-D	6/5/99	5.89	0.01	6.03	0.01

To test the idea of formaldehyde acting as a reducing agent making protactinium more particle reactive as well as enhancing sorption of thorium, a frozen sample from GOM was used in an experiment. This sample, once thawed was run in duplicate, one with formaldehyde added to a final concentration of 1% to mimic the HOT samples and one without. The sample without formaldehyde can also be used to compare against the initial values calculated 16 months prior. The results of this comparison (Table 4.7) show that there is no difference in the thorium log Kd values over time. However, the log Kd values of thorium for the frozen sample to which formaldehyde was added was significantly lower compared to the initial value, which does not explain why the log Kd values of the HOT sample values were so high. The protactinium data shows a marked increase in the log Kd over time (Table 4.7), but no difference between with and without formaldehyde treatments. At first,

this seems to dismiss the idea of formaldehyde as a reducing agent, promoting sorption but this experiment does not account for a kinetic effect. The HOT samples were preserved in formaldehyde and 5% NaCl for over 7 years, while the GOM experiment was only exposed for 2 days. Alternatively, the higher NaCl concentration might have caused coagulation of the colloidal fraction, thus causing higher log Kd values. Another interesting discovery is that the particle concentration for the frozen sample increased by a factor of 2 over the 16months it was frozen. The HOT samples also had over 7 times the particle concentration than the 2mg/L that was measured for GOM samples and also used for the BATS samples.

Table 4.7
Comparison of log Kd and log Kd_c values for ^{234}Th and ^{233}Pa from GOM sample, S2-90m, where initial was run onboard after collection, frozen refers to an aliquot frozen for 16 months, and frozen + 1% formalin refers to an aliquot frozen for 16 months after which the sample was thawed and formalin added for a final concentration of 1%.

	^{234}Th				^{233}Pa			
Condition	Log Kd	±	Log Kd_c	±	Log Kd	±	Log Kd_c	±
Initial	5.39	0.01	6.29	0.01	4.11	0.07	5.97	0.07
Frozen	5.37	0.05	5.92	0.09	5.14	0.07	5.50	0.08
Frozen + 1% formalin	3.94	0.20	6.57	0.09	5.20	0.07	5.82	0.08

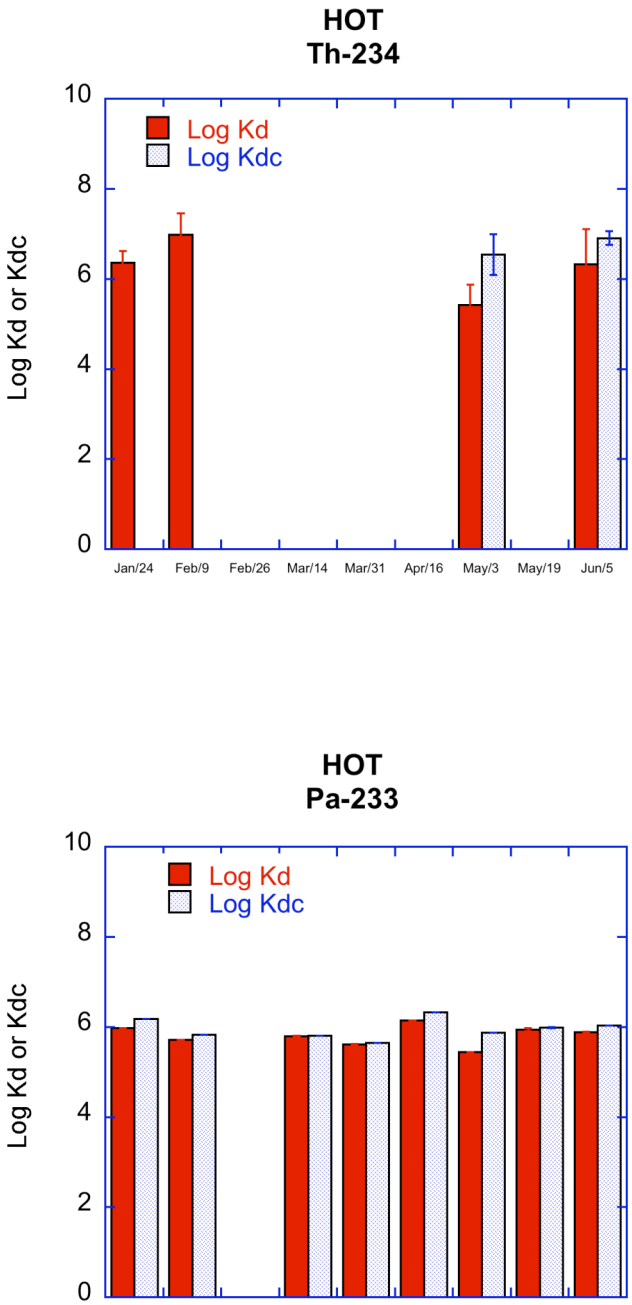

Figure 4.9. Log Kd and log Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu for sediment trap material collected at Hawaii Ocean Time Series (HOT) Aloha station where log Kd = fp/((fc+fd)*Cp) and log Kd_c =(fp+fc)/(fd*Cp)

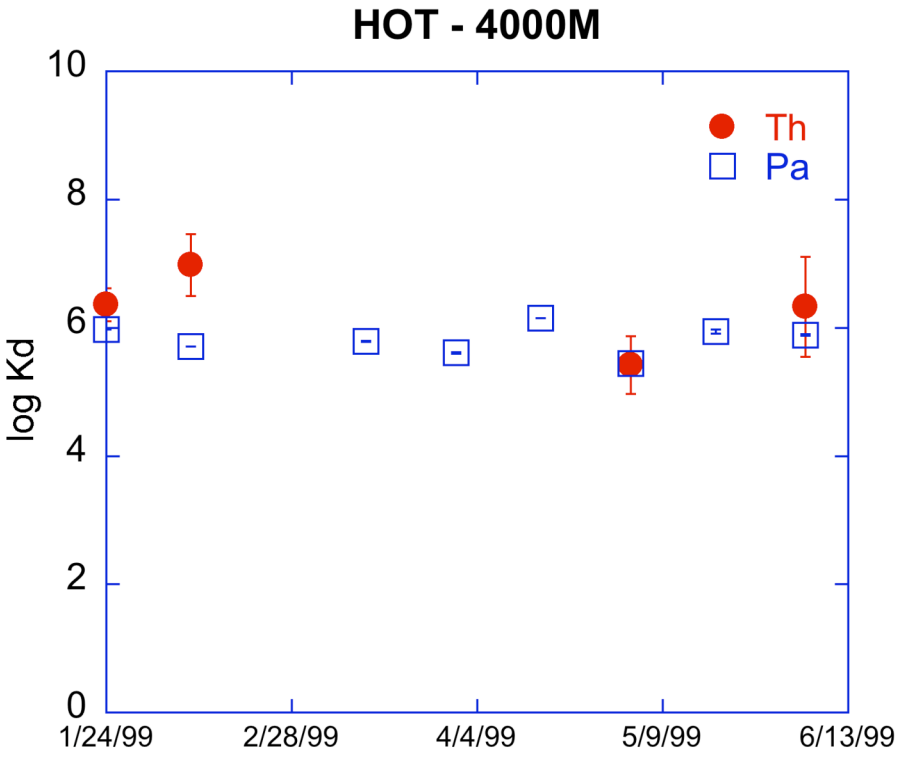

Figure 4.10. Log Kd values for HOT as a function of time.

4.5 Discussion

The original purpose of this study was to compare results from "fresh" material (GOM) against archived (BATS and HOT) material, to determine whether storage and preservation would affect the outcome. Unfortunately, such a comparison is not as straightforward as comparing the newly obtained GOM samples to the archived samples, in that they are collected from different depths in the water columns, which would also likely have affected their degradation status and chemical composition. GOM samples were all surface

samples collected at 140m or less. BATS samples were collected at 500m, 1500m, and 3200m, and all HOT samples were collected at a depth of 4000m. However, if degradation would have been important, one would expect the particle association to be highest in the freshest more labile material, next highest in the freeze-dried material and lowest in the frozen slurry that was thawed and stored in a refrigerator. Yet, this trend is not seen in comparing these sample sets. In fact, the opposite is seen, the Gulf of Mexico had lower log Kd values than the BATS samples, which had lower log Kd values than the HOT samples. As discussed above, one plausible explanation is the chemical interaction of the formaldehyde, a reducing agent, used to preserve the samples. Presence of a reducing agent could account for why the ^{233}Pa log Kd values are similar to those of ^{234}Th which would only be expected if the ^{233}Pa was present as Pa(IV). Though this was tested experimentally without the same findings, perhaps there wasn't a sufficient amount of time elapsed to successfully see the effect of the formaldehyde. Alternatively, the higher NaCl content of the sediment trap sample from HOT may be responsible.

Another purpose of this study is to compare data from this study to other similar studies. The material used here was naturally occurring material collected from sediment traps for which only limited compositional information is available. Yet, one can compare sorption values obtained here to other sorption studies. In the Gulf of Mexico sediment trap samples, we found lab-based log Kd values that range from 5.28 to 5.97 for ^{234}Th and 3.96 to 4.66 for ^{233}Pa (Tables 4.1 and 4.2). In archived sediment trap material from BATS log Kd

values range from 4.67 to 6.92 for ^{234}Th and 3.9 to 7.12 for ^{233}Pa (Tables 4.3 and 4.4) and in HOT samples 5.42 to 6.98 for ^{234}Th and 5.44 to 6.15 for ^{233}Pa (Tables 4.5 and 4.6). In laboratory conducted experiments, Guo et al. (2002) tested a variety of sorbents, both inorganic and organic, for sorption of thorium and protactinium. They found the log Kd values for Th to be lowest in chitin and amorphous silica (3.5 and 3.98 respectively) and highest on Carageenan (7.78). Protactinium, on the other hand was found to sorb less to calcium carbonate (log Kd 3.68) and chitin (log Kd 3.69) but its log Kd was also the highest on carageenan (log Kd 7.49). Geibert et al. (2004) examined sorption of ^{234}Th in filtered seawater to different minerals and found a mean log Kd value of 6.9 for smectite, 7.7 for MnO_2, 6.1 for opal, and 5.8 – 6.8 for $CaCO_3$. Since actinide affinity for specific sorbents, depending on their pretreatment and other factors, may differ, the log Kd values for these two studies are not necessarily in exact agreement with those from the work presented here.

Another means of looking at Th and Pa data is the fractionation of the Kd values or F(Th/Pa). Chase et al. (2002), Luo and Ku (2004), and Li (2005) have used a multiple correlation approach to deduce dominant mineral types that would be responsible for Th/Pa fractionation. F(Th/Pa) values for the different studies have been compiled in Table 4.8. A value for F(Th/Pa) of 1 would indicate there is no fractionation between thorium and protactinium. As can be seen from this compilation, the F(Th/Pa) values from this study are in general agreement, when the presence of organic matter associated with mineral

Table 4.8
Compilation of Kd data for sediment trap material and laboratory experiments, where F(Th/Pa) is the ratio of Kd values.

	Th	Pa	F(Th/Pa)
Study	Log Kd	Log Kd	
This Study			
GOM (average)			26.08
BATS (average)			2.67
HOT (average)			2.24[a]
SiO_2	5.54	4.39	14.16
SiO_2+EPS	5.74	4.34	25.20
$CaCO_3$	5.70	5.11	3.83
$CaCO_3$+EPS	6.58	5.26	20.52
Guo et al. 2004			
MnO_2	6.14	6.2	0.87
Fe_2O_3	5.83	5.15	4.79
$CaCO_3$	5.6	3.68	83.18
Humic Acid	5.58	4.31	18.62
Chitin	3.5	3.69	0.65
SiO_2	3.98	5.09	0.08
Carrageenan	7.78	7.49	1.95
Geibert &Usbeck, 2004			
Smectite	6.85	6.20	4.44
MnO_2	7.66	7.79	0.75
$CaCO_3$	6.86	5.23	42.35
Opal	6.08	5.70	2.40
Luo & Ku, 2004			
Lithogenics			0.05
Carbonate			0.1
Opal			4.8
Chase et al., 2002			
Overall	6.68	5.76	8.42
Opal	5.59	6.15	0.28
Carbonate	6.95	5.34	40.91
Luo & Ku, 1999			
Clay			~10.9
Biogenic silica			~1

[a] excludes single outlier of 18.62

phases is included. Furthermore, as shown in Figure 4.11, when thorium log Kd values are plotted against protactinium log Kd values, values to the right of the

1:1 line indicate an enhancement of thorium or lower affinity of protactinium to the particles. Though some of the archived (BATS and HOT) samples are on or very near the 1:1 correlation line, all of the GOM samples are clustered to the right of line. The fact that GOM samples contained fresher particulate material from the upper water column, while the other samples were from deeper waters could account for the higher sorption of thorium than protactinium.

Chase et al. (2002) determined an overall F(Th/Pa) of 8.42, 0.28 for opal and 40.9 for carbonate, thereby concluding that carbonate preferentially fractionates Th over Pa. Work by Guo et al. (2002) also demonstrated that calcium carbonate had the highest F(Th/Pa), with a value of 83, as compared to others sorbents such as silica (0.08), MnO_2 (0.87), Fe_2O_3 (4.79) and humic acid (18.6). Luo and Ku (2004) calculated F(Th/Pa) using endmember Kd values and determined ratios of 4.8 for opal, 0.1 for calcium carbonate and 0.05 for lithogenics and thus concluded that biogenic silica or opal was the most significant mineral type to cause fractionation of thorium over protactinium. Li (2005) determined that this discrepancy between Chase et al. (2002) and Luo and Ku (2004) is partially due to whether the data set from three regions is treated as one large set or assessed individually by region. Li (2005) also admits that this controversy ignores the contribution of organic components, which is not always valid.

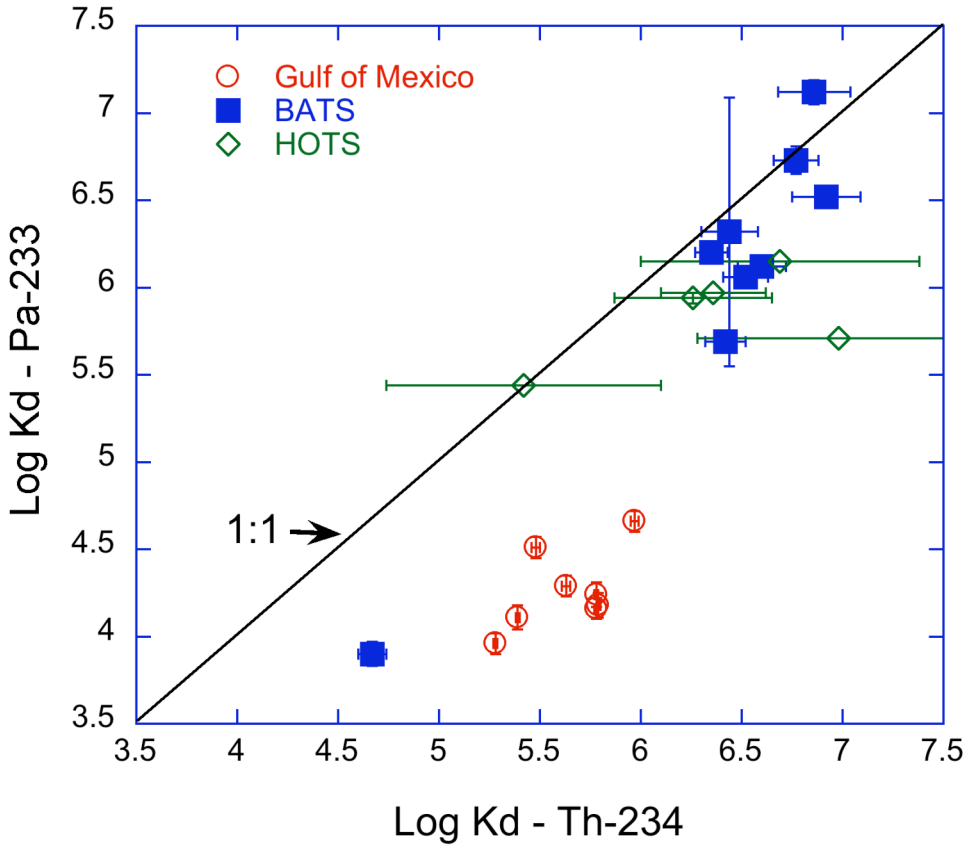

Figure 4.11. Log Kd values for ^{234}Th versus ^{233}Pa. A one to one correlation would indicate no fractionation.

Geibert and Usbeck (2004) confirmed the findings of Chase et al. (2002) and Guo et al. (2002) that sorption on to calcium carbonate resulted in the highest F(Th/Pa) values, with a range of 3.5-42, as compared to 4.4 for smectite, 0.75 for MnO_2, 2.4 for opal calculated from the mean of their reported Kd data. In this study, all sediment trap samples analyzed had a wide range for F(Th/Pa), i.e., 0.6 – 41.7.

Since the largest discrepancy appears to be between the F ratio for silica and calcium carbonate, these two sorbents were tested utilizing the same procedures for the sediment trap material. Our experimental results were more in line with the findings of Luo and Ku (2002). Our study showed that the amorphous silica used here had higher F(Th/Pa) values than those reported by others for opal, which may simply be a function of particle size or surface area. Yet, when both silica and calcium carbonate were studied with an associated organic colloidal phase, i.e., extracellular polymeric substances (EPS) from the bacterium *Sagittula stellata*, the results tell a different story. For both ternary systems (i.e., mineral/organic phase and radionuclide), enhancement in the F(Th/Pa) values are seen. This increase is from 14.2 to 25.2 for silica, and for calcium carbonate, the increase is even more dramatic, with an increase from 3 to 20.79. Both of these ternary values fit better within the range for this study of sediment trap material of this study than observed for the pure inorganic particles alone. These results are also most directly comparable to the average F(Th/Pa) of 26.08 seen in the Gulf of Mexico surface sediment trap samples and may indicate that sorption is controlled by interaction with an organic colloid, likely a biologically produced exopolymer that preferentially sorbs thorium.

Further investigation into the importance of the organic colloidal influence on the fractionation of thorium and protactinium can be seen if one tests for a correlation between the log Kd of thorium to the calcium carbonate content of the material. Such a correlation can be carried out for the BATS samples as calcium carbonate data is available. Figure 4.9 shows a positive

correlation between the log Kd of thorium and the calcium carbonate content for BATS samples. However, if one would extrapolate to 100% calcium carbonate one would expect a log Kd value of 8 or 9 for thorium, which is three orders of magnitude higher than what was found in this study and what is available from the literature. The separate laboratory experiment that was carried out resulted in a log Kd of 5.7, similar to a value of 5.6 by Guo et al. (2002). Both of these values are slightly lower than the values reported by Chase et al., 2002 (6.95) and Geibert & Usbeck, 2004 (6.85). Yet all these values fall well below the extrapolated value for 100% calcium carbonate. Thus, one may conclude that there is something else occurring in conjunction with the calcium carbonate. Data on composition of total carbohydrates (TCHO), protein and uronic acids (URA), normalized to organic carbon (C.-C. Hung, unpublished data), were compared with the calcium carbonate data. Unfortunately, information on organic components was not acquired on the same samples that sorption experiments were conducted on, because the compositional analysis required all or nearly all of the sample. Of the three organic constituents analyzed, only total carbohydrate content showed a significant and positive correlation with calcium carbonate content (Figure 4.9) From this, one can conclude that there is some organic substance rich in polysaccharides co-occurring with the calcium carbonate. In aquatic systems, this is reasonable as calcium carbonate is biologically produced and the organisms producing the calcium carbonate could excrete such an organic substance adhering to $CaCO_3$, or bacteria responsible for producing EPS may colonize this material. Though data on total carbohydrates

(TCHO) is available for GOM samples (Chen Xu, unpublished data), $CaCO_3$ content on sediment trap samples is not. Therefore, the same correlation could not be demonstrated with this sample set. Furthermore, while the log Kd values for ^{234}Th, determined in the field and lab, are of the same order of magnitude, and TCHO and URA data are available, with significant correlations were obtained between lab and field, or with compositional data (not shown).

4.6 Conclusions

Attempts to compare fresh and archived sediment trap samples gave somewhat ambiguous results, possibly due to many differences between the Gulf of Mexico sample set and archived samples. Not only were the depths of these samples wide ranging, methods of preservation may have altered the outcome of calculated particle-water partitioning coefficients. However, several observations can still be made regarding sorption to sediment trap material with regards to thorium, protactinium and their fractionation. Log Kd values for these samples are comparable with those reported by others (Chase et al., 2002, Luo and Ku, 2004, Li, 2005) and for laboratory experiments conducted on laboratory grade sorbents (Guo et al., 2002 and Geibert and Usbeck, 2004).

The average fractionation of thorium and protactinium, F(Th/Pa) was found to be much higher in fresh sediment trap samples (~26 for Gulf of Mexico) than for archived ones (~2.5 for BATS and HOT). Not only were the Gulf of Mexico samples analyzed right after collection, but they were taken from surface waters of 140m and shallower. Previous studies (Chase et al. 2002, Guo et al.,

2002, and Geibert and Usbeck, 2004) have suggested that enhanced scavenging of thorium on calcium carbonate is the driving mechanism for this fractionation. Yet, values of log Kd of 8 to 9 for Th, and around 8 for Pa, when extrapolated to 100% calcium carbonate, are three orders of magnitude higher than those observed in laboratory experiments. This suggests that there is another factor involved in this Th/Pa fractionation. Experiments conducted here clearly demonstrate that a fractionation similar to the field data is only seen in the presence of an organic third phase. Correlations of log Kd values with organic compositional data (Hung, pers. communication) suggest that this organic compound contains polysaccharides that co-occur with calcium carbonate. Therefore, it is believed that the presence of a saccharide-rich organic component, most likely from exopolymers produced biologically in surface oceans that are degraded over time and with depth in the water column, is primarily responsible for the fractionation seen in field samples.

5. THORIUM, PROTACTINIUM, AND PLUTONIUM SORPTION ON SILICA AS A FUNCTION OF IONIC STRENGTH AND pH USING "BETTER BUFFERS"

5.1 Overview

Thorium, protactinium and plutonium sorption onto silica particles were studied as a function of ionic strength and pH, using a series of non-complexing buffers, with and without extracellular polymeric substances (EPS) present. Very low concentrations of 10^{-15} to 10^{-12} M of the actinides were used to mimic environmental conditions. For all three actinides, change in ionic strength did not influence the sorption indicating formation of inner-sphere complexes. Thorium and plutonium showed a clear sorption edge between pH values of (2.5 to 4). The sorption edge for protactinium, which must be below pH of 4, was not determined as no data were acquired below that pH. Silica dissolution increases with increasing pH and can become problematic at pH 10 at the concentrations of 0.5g/L used here. Lack of acquired thermodynamic data prevented modeling of the data presented here, but comparison of sorption studies on silica under similar conditions, indicate that surface complexation modeling (SCM) could be completed on this data set.

5.2 Introduction

The mobility of metal ions in the aquatic environment is controlled by chemical speciation, i.e., complexation to solutes and surfaces, which change with solution conditions, e.g., pH and ionic strength (Stumm and Morgan, 1996).

A systematic study of surface complexation or sorption of metals as a function of ionic strength and pH offers insight as to the type of chemical interaction taking place between the metal and mineral surface. For example, if a change in ionic strength changes the sorption of an actinide that is evidence that the reaction to the surface ligand is weak and sensitive to its surroundings. Conversely, if a change in ionic strength results in no change in the sorption reaction implies that the actinide ion is bound more strongly and is present as an inner sphere complex. Assessing sorption as a function of pH can result in detailed information about the bonding environment, i.e., the kinds and bond strengths of the surface ligand. In case of a cation, sorption curve is expected to increase with increasing pH because of less H^+. In the case of an anion, sorption is expected to decrease with increasing pH due to OH^- competition. Systematic experimental studies allow for modeling of the sorption behavior that yield thermodynamic data on the multitude of surface and solution reactions. Though there have been many studies to systematically investigated the pH dependence of the sorption of actinides on mineral surfaces, none have utilized buffers for batch experiments, as was done here. As shown in section 2, neutralization of an acidic tracer in a near neutral system can greatly affect the results of particle-water partitioning experiments. This study, though not restricted to near neutral pH, utilized a series of non-complexing buffers in solution to maintain constant pH thereby limiting short-term micro pH gradients after base addition to the solution and thus, possible experimental artifacts due to irreversible formation of colloidal impurities from reagents that

can strongly comples particle-reactive actinide ions fM and pM concentrations.

In 1966, Good et al. introduced 12 hydrogen buffers over the neutral pH range touted as being useful due to their being biologically unreactive. Over the next decade or so other hydrogen ion buffers were introduced leading to 20 buffers in total. Yu et al., 1997 identified that all but three of these 20 Good's buffers form metal complexes. They studied the metal complexation and proposed a series of noncomplexing buffers useful over a pH range of 3-11. Since the purpose of this study is to systematically investigate sorption of actinides on inorganic particles, the series of buffers proposed by Yu et al., 1997 proved more useful in this case than the original biologically unreactive Goods' buffers referred to as "Better buffers" by GFS chemicals. Given a sorption edge of Th on silica between 2-4 (Osthols, 1995, Weijuan and Zuyi, 2002, Reiller et al., 2003), a sorption experiment for Th was also conducted without buffers present to obtain a data value within this range, i.e., pH of 2.5.

5.3 Methods

Sorption experiments were carried out in batch fashion. Centrifuge tubes (50ml) were used as the vessels, to which the appropriate buffer solution was added. To each tube the appropriate tracer, ^{233}Pa added in equilibrium with ^{237}Np (10^{-15} M), ^{234}Th (10^{-14}M), or ^{240}Pu (10^{-12}M) was added. The oxidation state of the ^{240}Pu was determined following the procedure of Saito and Choppin, 1983. It was determined that $\geq$ 75% was in the (IV) oxidation state and up to 20% was found in the organic/aqueous interface, of which some or all could belong to the

IV (Appendix B). ^{233}Pa was assumed to be V (Pal'shin et al., 1970) and ^{234}Th as IV. The tube was mixed and the pH measured. The tubes were mixed on a shaker for 48 hours after which time the pH was measured and the samples were then fractionated. Size fractionation was carried out first by 0.4μm filtration. The filtrate was subsequently ultrafiltered using a 1kDa ultrafilter in a stirred cell ultrafiltration apparatus. The ultrafiltration separated the less than 0.4 μm into a) 1kDa – 0.4 μm and b) <1kDa fractions. ^{234}Th and ^{233}Pa were counted on a well germanium counter at 63keV and 312 keV, respectively. After physical separation, ^{242}Pu tracer was added to the plutonium samples, which were processed through ion exchange columns followed by lanthanum fluoride precipitation and alpha counting.

Solutions were made using 0.1M $NaClO_4$ solution with a buffer concentration of 50mM to correspond to the work done with Pu (section 3) using Tris/HCl. The solution pH was adjusted using trace metal acid or sodium hydroxide to achieve the desired pH. A test on the stability of pH was conducted with the solution and acid concentrations corresponding to that added with the actinide tracers. The buffers and their corresponding intitial pH values used in this study are listed in Table 5.1.

As the primary focus of this research is the sorption of actinides on inorganic particles in the presence of an organic colloidal third phase. A ternary system and it's corresponding binary end members will be studied here. For the organic colloid alone, 5mg/L of extracellular polymeric substances (EPS) from a bacterial culture of *Sagittula stellata* was used that was supplied by Chen

Xu. For silica, lichrosorb 60 from EMD (formerly GFS chemical), was used at a concentration 0.5g/L. The silica particles that were used have a mean size of 5μm and surface area of 500 m^2/g. The ternary system will be a combination of the EPS and silica at the same concentrations used for the endmembers.

Table 5.1
List of buffers (GFS chemicals) and corresponding initial pH.

Buffer	Full name	pH
PIPPS	Piperazine-N,N′-Bis(3-Propanesulfonic acid)	4.12
DEPP	N,N′-Diethylpiperazine	5.02
MES	2(N-Morpholino)ethanesulfonic acid	6.22
MOPS	3-(N-Morpholino)propanesulfonic acid	7.28
PIPES	Piperaczine-N,N′-Bis(2-ethansulfonic acid)	8.48
PIPBS	Piperazine-N,N′-(4-butanesulfonic acid)	9.12
TEEN	N,N,N′,N′-Tetraetylethylenediamine	10.88

In addition to data being assessed in terms of the fraction sorbed to the silica (fp), the particle- or (colloid-) water partioning coefficient or Kd can be calculated from the fraction of the activity in the different frations: particulate (fp), colloidal (fc) and (truly) dissolved (fd) fractions, and the particle concentration (Cp), i.e.,

$$Kc = fc/\{(fd)*Cp\}$$

$$Kd = fp/\{(fc+fd)*Cp\}$$

In order to better assess the colloidal contribution to particle-water partitioning, the partitioning coefficient (Kd_c) was also calculated by including the colloidal fraction in the particulate fraction, i.e., that fraction that is retained by an ultrafilter, i.e.,

$$Kd_c = (fp+fc)/\{fd*Cp\}$$

Where fp = fraction on the particles (e.g., silica); fc = fraction retained by 1kDa ultrafilter (retentate); fd = fraction that passes through a 1kDa ultrafilter (permeate); Cp = particle concentration (g/mL); Kd = particle-water partitioning coefficient; Kd_c = particle & colloid-water partitioning coefficient including the retentate in the particulate fraction.

Table 5.2
^{240}Pu, ^{234}Th, and ^{233}Pa log Kc values for EPS from *Sagittula stellata*, log Kd and Kd_c values for silica and log Kd and log Kd_c values for silica and EPS from *Sagittula stellata* for varying ionic strengths of solution ($NaClO_4$)

I	SS Log Kc	±	Si Log Kd	±	Si Log Kd_c	±	SiSS Log Kd	±	SiSS Log Kd_c	±
^{240}Pu										
0.001M	7.05	0.11	4.05	0.04	4.23	0.04	4.49	0.05	4.65	0.05
0.01M	5.69	0.05	4.79	0.06	5.12	0.09	5.10	0.12	5.58	0.19
0.1M	5.39	0.05	4.75	0.07	4.92	0.06	4.66	0.06	4.81	0.06
0.7M	5.03	0.06	4.73	0.06	5.02	0.08	4.89	0.07	5.00	0.08
^{234}Th										
0.001M	6.44	0.04	5.30	0.08	5.90	0.30	4.96	0.05	5.54	0.15
0.01M	6.35	0.04	5.57	0.09	6.47	0.34	5.46	0.10	6.28	1.34
0.1M	5.84	0.05	5.54	0.11	6.08	0.55	5.74	0.18	6.64	0.19
0.7M	6.43	0.06	6.37	0.65	[a]	[a]	5.44	0.08	5.59	0.10
^{233}Pa										
0.001M	5.96	0.02	4.45	0.04	4.51	0.04	4.28	0.04	4.48	0.04
0.01M	6.50	0.04	4.56	0.03	4.63	0.03	4.40	0.03	4.46	0.03
0.1M	5.26	0.05	4.39	0.04	4.43	0.04	4.34	0.02	4.48	0.03
0.7M	5.92	0.04	4.50	0.06	4.56	0.06	4.39	0.05	4.52	0.06

[a] no activity in the permeate fraction

5.4 Results and discussion

5.4.1 Ionic strength effect

All three actinides, ^{234}Th, ^{233}Pa, and ^{240}Pu were first studied as a function of ionic strength (Table 5.2, Figures 5.1-5.3). All three actinides show little or no

effect of the ionic strength on the resulting log Kc, log Kd or log Kd_c values. Lack of influence of ionic strength of solution on the sorption is indicative of the formation of inner sphere complexes. This is consistent with findings of thorium(IV) on hematitite (Quigley et al., 1996), on TiO_2 (Jakobsson, 1999), on alumina (Hongxia et al., 2006), on alumina and silica (Weijuan, and Zuyi, 2002), and on silica (Chen and Wang, 2007). This is also consistent with the findings of Sanchez et al., 1985 for plutonium (IV) and (V) on goethite. No published studies of ionic strength effects on sorption of protactinium were found for comparison.

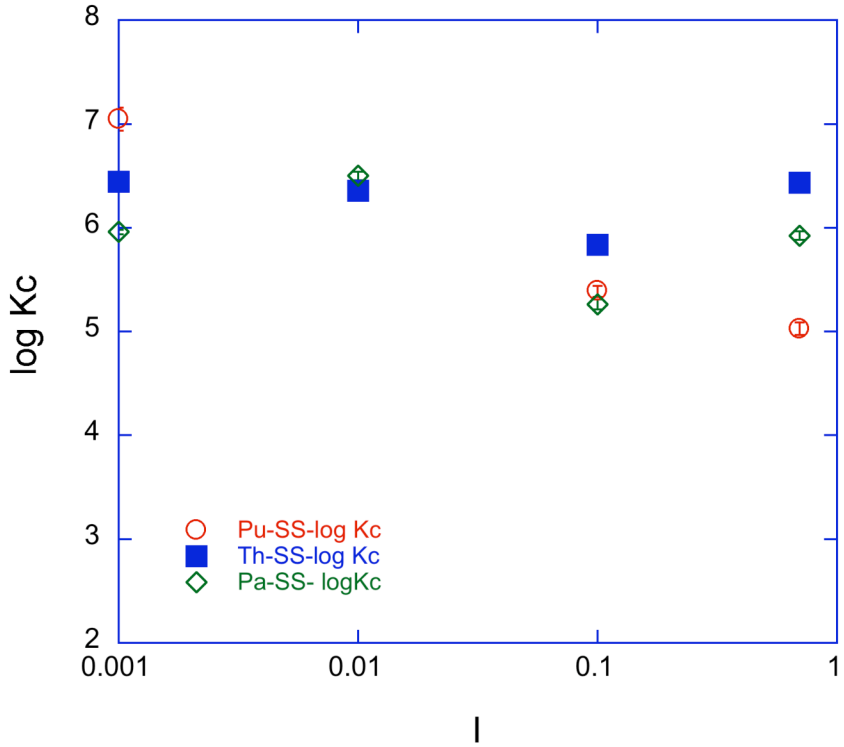

Figure 5.1. Log Kc values for ^{234}Th, ^{233}Pa and ^{240}Pu sorbed on EPS from *Sagittula stellata* as a function of ionic strength of solution ($NaClO_4$).

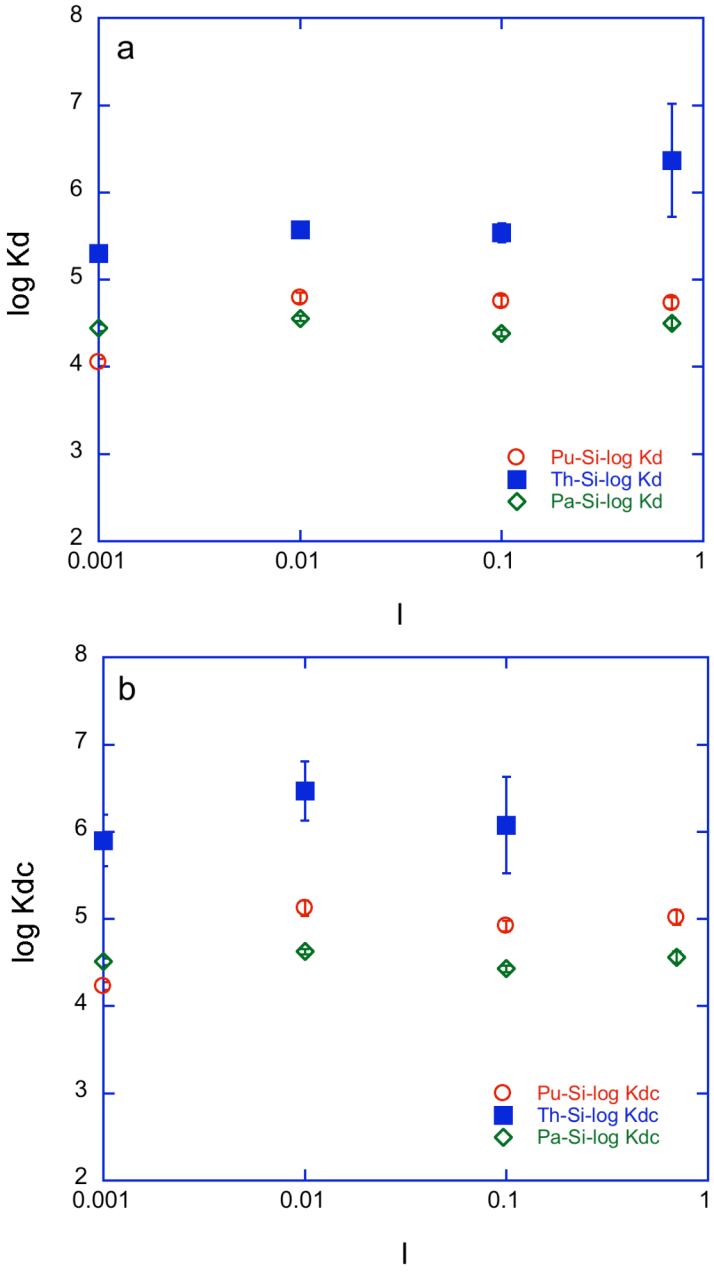

Figure 5.2. Log Kd and log Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu sorbed on silica particles as a function of ionic strength of solution ($NaClO_4$).

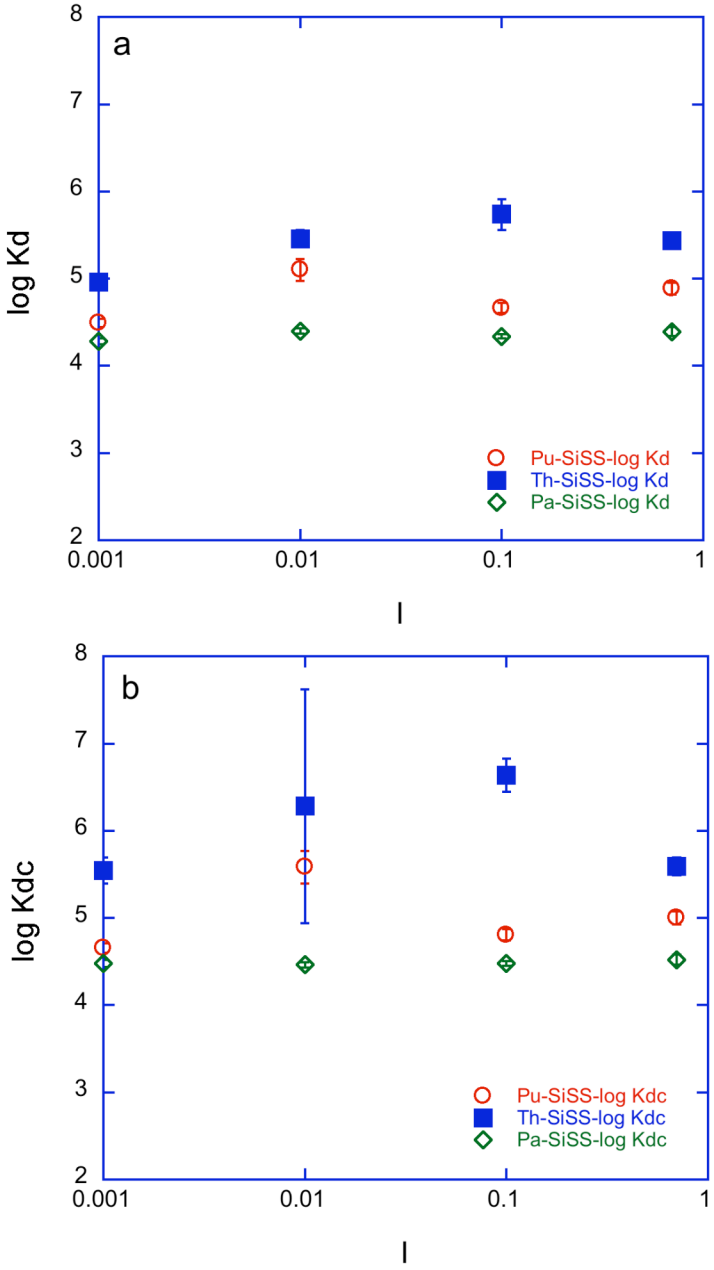

Figure 5.3. Log Kd and log Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu sorbed on silica particles and EPS from *Sagittula stellata* as a function of ionic strength of solution ($NaClO_4$).

5.4.2 pH dependence

The sorption of thorium, protactinium and plutonium as a function of pH provides more detail than that with ionic strength (Table 5.3). The lowest pH of the buffers utilized by this study is pH 4. Since the sorption edge starts lower than that (2-3), one point was acquired for thorium and plutonium in which no

Table 5.3
^{240}Pu, ^{234}Th, ^{233}Pa log Kc values for EPS from *Sagittula stellata* (SS), log Kd and Kd_c values for silica (Si) and log Kd and log Kd_c values for silica and EPS from *Sagittula stellata* (SiSS) as a function of pH in 0.1M $NaCl0_4$ solution with 50mM "better buffers".

	SS		Si				SiSS			
	Log		log		log		log		log	
pH	Kc	±	Kd	±	Kd_c	±	Kd	±	Kd_c	±
^{240}Pu										
2.5			2.5	0.11						
4	5.87	0.06	3.36	0.03	3.92	0.03	3.54	0.03	4.29	0.04
4.75	5.38	0.05	4.33	0.05	4.75	0.07	4.55	0.06	4.98	0.09
5.98	5.83	0.06	4.33	0.06	4.48	0.06	4.56	0.07	4.74	0.09
6.88	5.26	0.05	4.71	0.06	5.04	0.08	4.46	0.08	4.77	0.09
8.2	5.87	0.05	4.77	0.07	5.01	0.09	4.39	0.07	4.98	0.11
10.12	5.09	0.06	4.75	0.07	5.00	0.09	4.77	0.07	5.12	0.08
^{234}Th										
2.5			3.10	0.06	3.98	0.08				
4	6.21	0.10	2.80	0.04	3.74	0.04	2.30	0.08	4.05	0.09
4.75	6.29	0.23	4.50	0.08	5.04	0.34	4.44	0.05	5.30	0.44
5.98	5.58	0.15	5.62	0.68	[a]	[a]	4.17	0.36	4.35	0.73
6.88	5.36	0.11	[a]	[a]	[a]	[a]	5.04	0.09	[a]	[a]
8.2	5.18	0.12	5.06	0.24	[a]	[a]	4.61	0.05	[a]	[a]
10.12	7.46	0.14	2.46	0.05	5.55	0.77	2.62	0.04	5.55	0.37
^{233}Pa										
4	6.14	0.06	4.30	0.06	4.32	0.04	4.27	0.03	4.59	0.05
4.75	5.87	0.06	4.85	0.01	4.83	0.08	4.48	0.04	4.82	0.06
5.98	5.21	0.05	4.61	0.10	4.65	0.06	3.75	0.02	4.26	0.04
6.88	5.14	0.05	4.52	0.05	4.59	0.05	3.91	0.03	4.39	0.04
8.2	5.06	0.04	4.47	0.05	4.57	0.05	3.99	0.02	4.52	0.05
10.12	6.40	0.06	2.76	0.03	3.90	0.03	2.75	0.02	4.03	0.03

[a] no activity in the permeate fraction

buffer was used and the pH of the solution was 2.5. Due to limitations on the amount of tracer, protactinium could not be measured below pH 4 so the sorption edge could not be clearly defined.

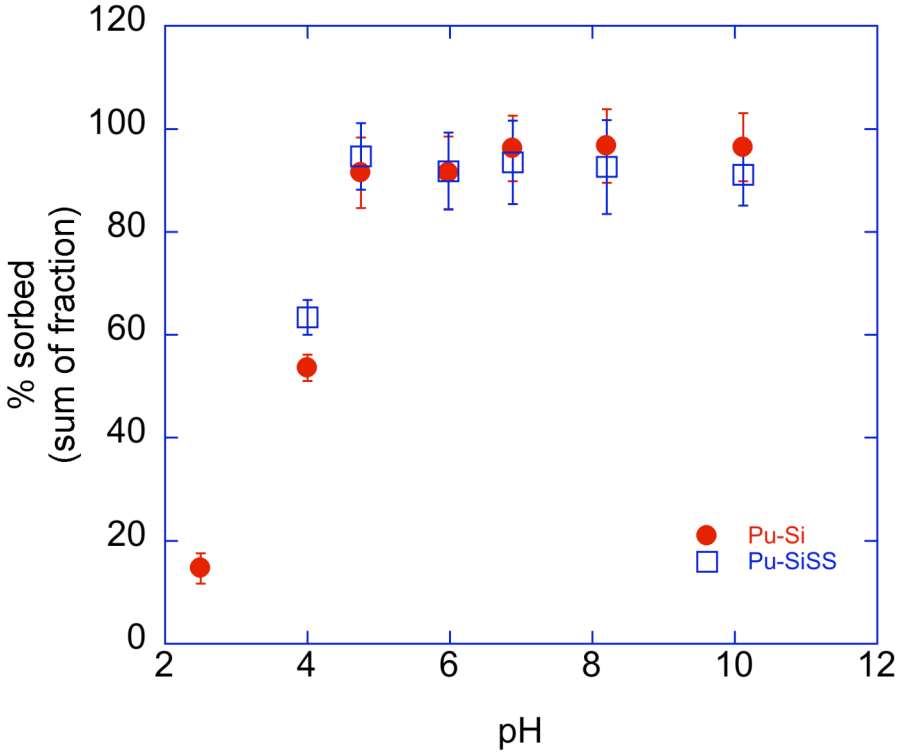

Figure 5.4. Percent sorbed onto silica (Si) or silica and EPS from *Sagittula stellata* (SiSS) for ^{240}Pu using non-complexing buffers to maintain pH. A silica concentration of 0.5g/L and EPS concentration of 5mg/L were used.

5.4.2.1 Plutonium

Plutonium exhibited a typical cation sorption behavior with low sorption at low pH, a rapid increase (sorption edge = pH 2.5-4.75), and reaching a plateau above the sorption edge (Figure 5.4). The location of the sorption edge can be

compared with findings of others, even though it is difficult to find a study with the same conditions (silica, actinide concentrations etc.). Strictly speaking the sorption edge is defined where there is a marked increase in cation sorption with pH and includes the pH where 10% is sorbed as the lower limit of the sorption edge and the pH where 90% sorbed as the upper limit. This is similar to the sorption edge seen by Sanchez et al. 1985 for Pu(IV) on goethite. The presence of EPS from *Sagittula stellata* appeared to have little effect on the sorption. Log Kc values for the binary system of EPS/Pu showed no significant change with pH (Figure 5.5). No effect of EPS was seen on the log Kd or log Kd_c values for the Si/Pu binary system (Figure 5.6), nor for the Si/EPS/Pu ternary system (Figure 5.7).

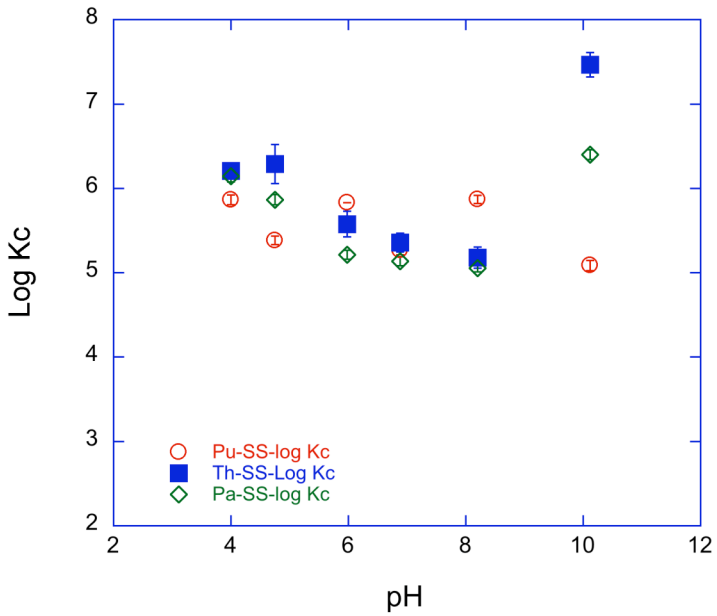

Figure 5.5. Log Kc values for ^{234}Th, ^{233}Pa and ^{240}Pu sorbed on EPS from *Sagittula stellata* as a function of pH.

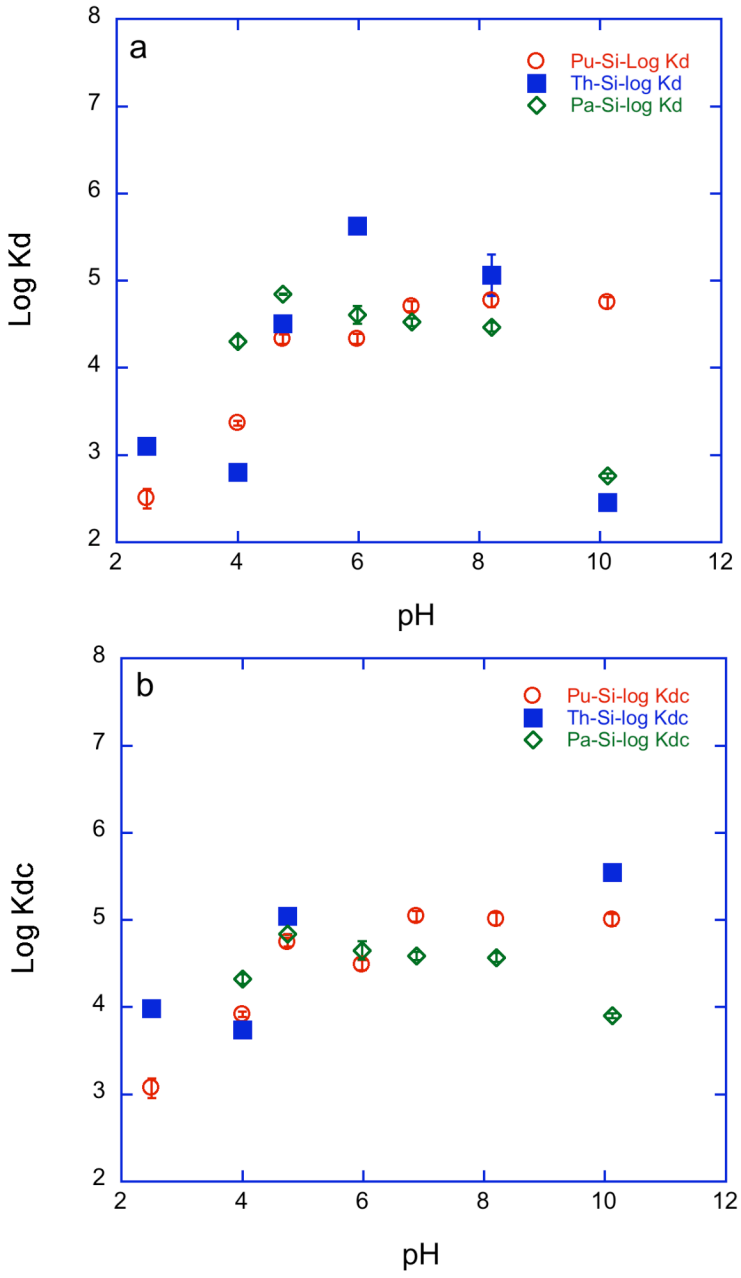

Figure 5.6. Log Kd for and log Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu sorbed on silica particles as a function of pH.

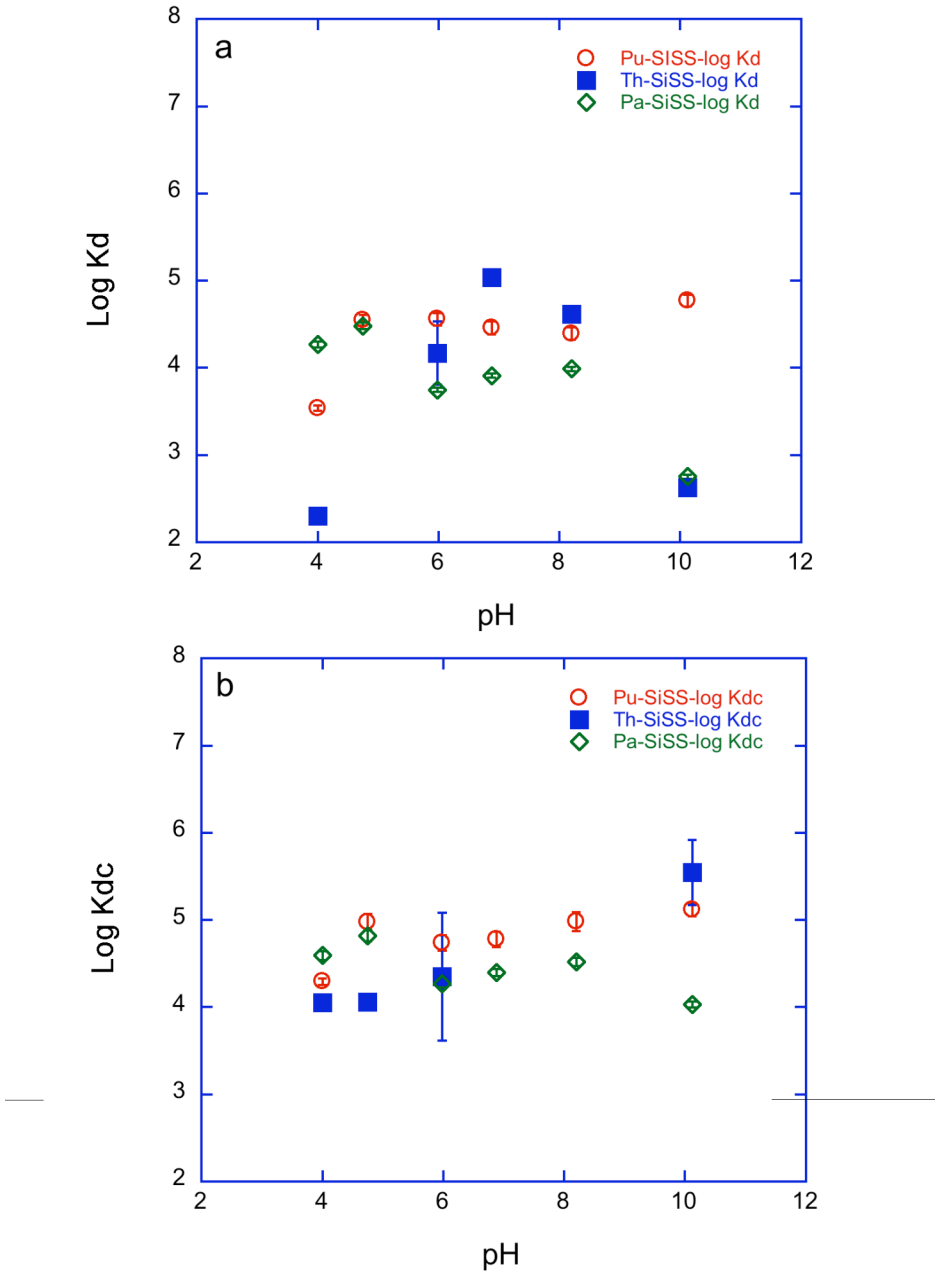

Figure 5.7. Log Kd and Kd_c values for ^{234}Th, ^{233}Pa and ^{240}Pu sorbed on silica particles and EPS from *Sagittula stellata* as a function of pH.

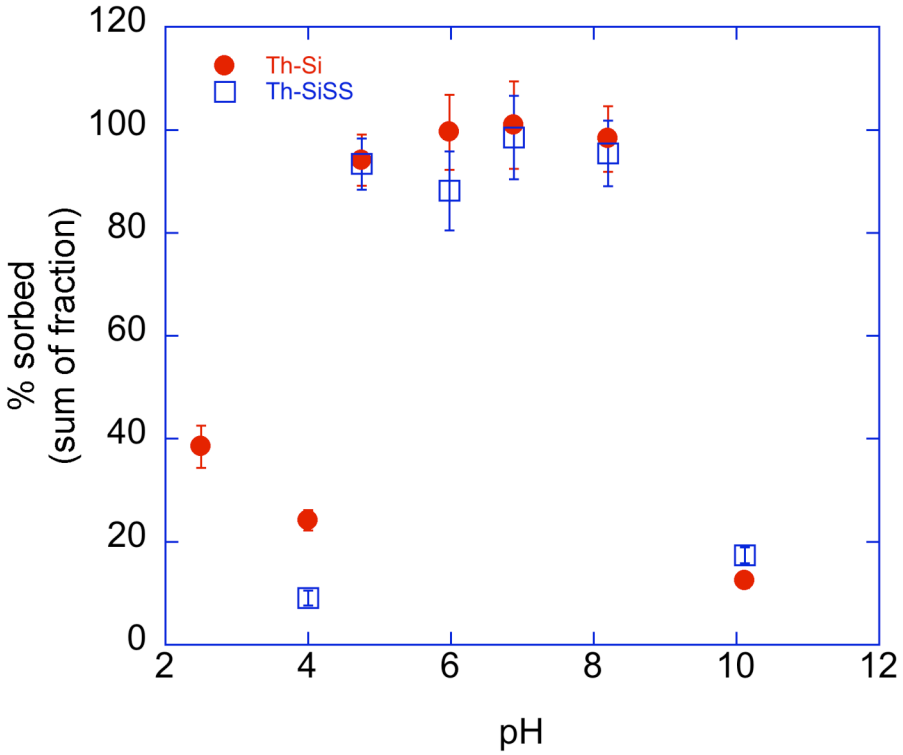

Figure 5.8. Percent sorbed onto silica (Si) or silica and EPS from *Sagittula stellata* (SiSS) for ^{234}Th using non-complexing buffers to maintain pH. A silica concentration of 0.5g/L and EPS concentration of 5mg/L were used.

5.4.2.2 Thorium

Thorium exhibited cation behavior at low pH to near neutral pH as is commonly seen in sorption studies (Hunter et al. 1988, Osthols, 1995, Jakobbson 1999). The sorption edge for thorium is found between pH 2.5 and 4. This is similar to sorption edge at pH 2-4 of others (Osthols 1995, Reiller et al., 2003). The percent of thorium sorbed looked similar to that of plutonium with two exceptions (Figure 5.8). The pH 2.5 is slightly higher than the pH 4 and there is a marked drop in sorption at pH 10. The log Kc of thorium showed a significant

increase at pH 10 indicative of a high colloidal association (Figure 5.5). Thorium was not quantifiable with an acceptable precision for pH 6-8, in the silica/Th system due to the fact that its activity in the permeate fraction was near the detection limit. Qualitatively, one can see that if log Kd values could be calculated, they would be near 5. The log Kd of thorium and silica shows a marked drop off at pH 10, which is not reflected in the log Kd_c value (Figure 5.6). Such a pattern for the binary Si/Th system might indicate that the thorium, though not associated with the particles is largely associated with the colloidal fraction. A similar trend is seen in the ternary Si/EPS/system (Figure 5.7). The main difference is that in the ternary system a colloidal fraction is added, while in the binary system, it is not. This raises the question of what is the colloid in the binary system and where does it come from if not introduced in the experimental system and it is not seen in the case of plutonium.

The solubility of silica increases dramatically at high pH i.e. between 9 and 10, and is about 500 mg/L at pH of 10.1 (Iler, 1979). A test of silica dissolution at pH 10 was run in duplicate. This test was run under the same conditions as the sorption experiment, except nitric acid was used in place of the tracer. Test run #1 had a 72% loss in weight of silica, when the pre-weighed, dried filter was measured on the analytical balance. In test #2 there was visible silica in the bottom of the centrifuge just prior to filtration, which likely indicates that the silica was never completely resuspended. If this was the case, most of the silica would not be exposed to the high pH solution and a variable dissolution would be expected. This indeed is the case here as the silica loss was

only 28% of the initial silica concentration. Since the plutonium tracer experiments were run separately from those with thorium and protactinium tracers, the silica in the thorium and protactinium experiment may have been mostly dissolved as in test case #1 and the plutonium may not have been completely resuspended as in test case #2. Quantatively, one could see that if 99% of the silica was dissolved at pH 10, which is certainly possible given the solubility of silica, the log Kd calculated for the corrected particle concentration, Cp, would become ~4.5 more in line with what would be expected. Silica dissolution was not a problem at pH values lower than 10. Tests of silica dissolution showed an average 20-30% dissolution but this decrease in particle concentration (Cp) translates into less than 0.1 in the log scale which is generally smaller than the propagated error. Furthermore, the unaffected value of log Kdc can be attributed to the formation of the polysilicate complexants for Th. This also confirms the finding in section 1, in which the thorium was more sensitive to silicate impurities form storage in glass vials resulting in lower particle association than was plutonium.

5.4.2.3 Protactinium

The amount of Protactinium sorbed to silica with and without EPS is shown in Figure 5.9. This could be due to lack of data below pH 4 or more likely that the protactinium, presumably in the +5 oxidation state did not behave similarly to its tetravalent counterparts. A lack of sorption curve was also seen by Bradbury and Baeyens, 2006 with the sorption of Pu(V) on montmorillonite but predict a sorption edge between pH 2-4 using a simple 2site protolysis non-

electrostatic surface complexation and cation exchange model. The log Kc value (Figure 5.5) for protactinium followed a similar pattern as that of thorium. Though the colloidal association at pH 10 was not as high as that for the thorium. The binary system Si/Pa showed no change with pH with the exception of pH 10 which found much lower and near the unexpected low log Kd of thorium (Figure 5.6). The results from the ternary system Si/EPS/Pa (Figure 5.7) looked very similar to that of the binary system, indicating no significant effects of EPS on protactinium sorption. Because protactinium and thorium were run and analyzed together and separately from the plutonium, this lends more credence to the idea that enhanced dissolution of silica, which is about 500mg/L (Iler, 1979) at pH 10.1, resulting in formation of polysilicates in solution. This explains the unexpected low log Kd values due to a gross overestimate of the particle concentration. Furthermore, absence of a drop in the log Kd_c value which includes the colloidal fraction with the particulate indicates a strong association with colloids, which can be attributed to the formation of the polysilicate complexants for both Pa and Th.

5.4.3 Comparison with other sorption studies

The modeling of the two binary and single ternary systems was not attempted here due to lack of information on the silica and EPS used. However, one can see from the literature how this can be done descriptively. There have been many studies looking at the sorption of silica and several that have looked at the sorption of thorium in particular. The results from this study can be directly compared to those of Reiller et al. (2003), who worked with silica

particles of 0.3 meq/g surface site concentrations, and those of Östhols (1995), who used 0.5 meq/g silica particles with a specific surface area about 200 m^2/g,

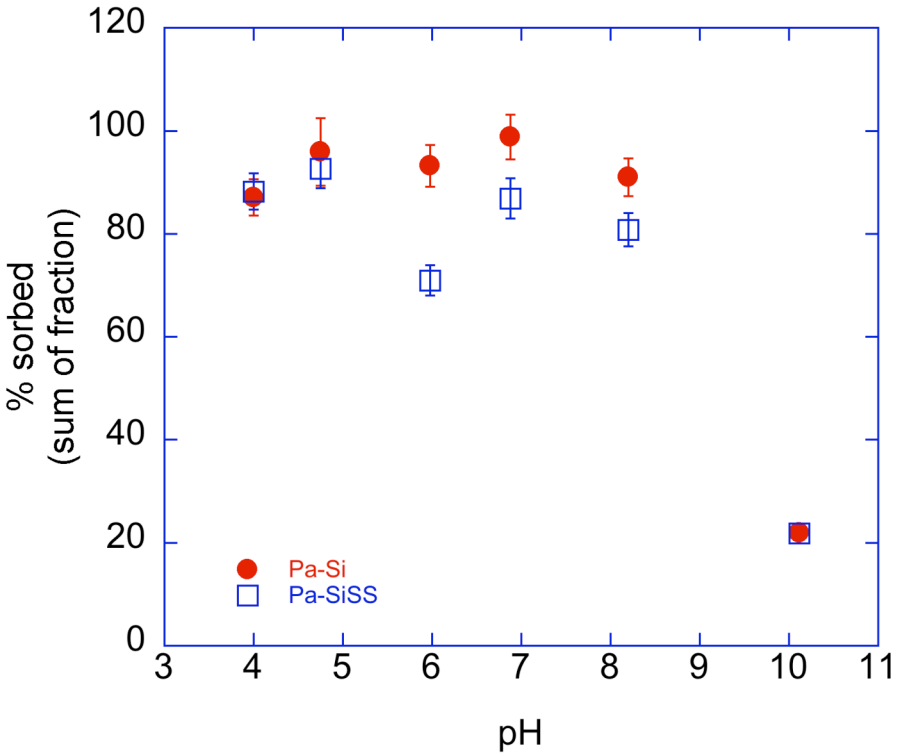

Figure 5.9. Percent sorbed onto silica (Si) or silica and EPS from *Sagittula stellata* (SiSS) for ^{233}Pa using non-complexing buffers to maintain pH. A silica concentration of 0.5g/L and EPS concentration of 5mg/L were used.

both silica particles likely to those that were used in this study, which had 500 m^2/g specific surface area. Figure 5.10 shows the log Kd versus pH for this study, as well as log Kd values taken from data in two studies, Osthols, 1995 and Reiller et al., 2003, that utilized similar conditions to this study. Plutonium data has been included in Figure 5.10, because of the similarity in chemical behavior of Th(IV) and Pu(IV), and the suspect data points for thorium at pH 4 and 10

discussed earlier. Data from Osthols, 1995 was only acquired for low pH values, but good agreement can be seen with the log Kd values at pH <4. Osthols used much higher Th(IV) concentrations than Reiller, 2003 (10^{-6} M as compared to 10^{-12}M), but both successfully used a surface complexation model to find a good fit between experimental and model data. However, because of the thorium concentration difference, Osthols, 1995, suggests a bidentate sorption whereas monodentate surface complexes more aptly describe by Reiller et al., 2003. Figure 5.10 shows the comparison of Osthols, 1995 log Kd data for low pH, log Kd data for Reiller et al., 2003 and Pu and Th data form this study. One can see that, although low pH data is lacking from this study, the trends are very similar to the others shown here. This similarity indicates that the series of buffers are suitable for sorption studies.

Most studies looking at the effects of organics on sorption have focused on the humic (Reiller et al., 2005; Reiller et al., 2003) or fulvic (Hongxia et al., 2006; Wang, et al., 2001) acids or both (Chen and Wang, 2007). Generally, humics and fulvics are better characterized than naturally occurring organic matter. Murphy et al., 1999 compared the sorption effects of well characterized humic acid to colloidal organic matter extracted from the ocean. Their study compared the sorption of the organics on a metal oxide surface but the comparison conditions were not identical. However, one can still see that the behavior is similar for the two compounds. For example Reiller et al (2003) simplified the ternary system by ignoring interactions between humic acids and silica. An assumption, which the authors admit is only valid at higher pH

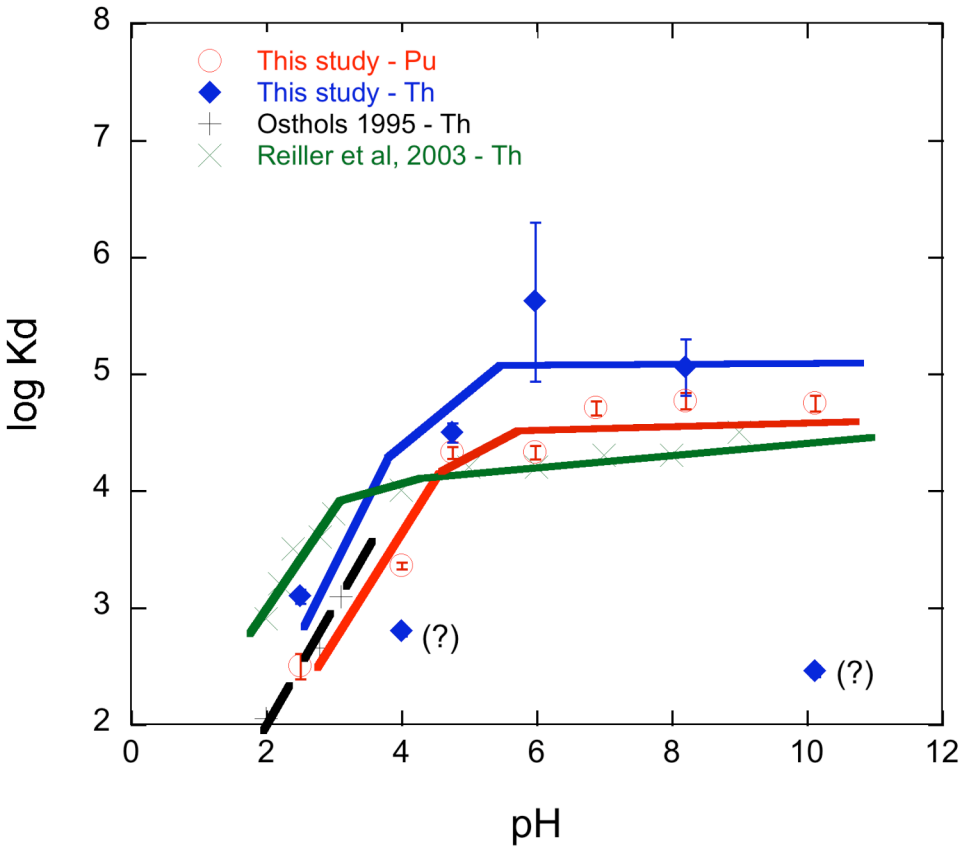

Figure 5.10. Comparison of log Kd values calculated in this study (0.5g/L silica 10^{-14} M ^{234}Th, I= 0.1M $NaClO_4$), Reiller et al. 2003 (0.25g/L silica, 10^{-12} M Th, and 0.1M $NaClO_4$ and Osthols 1995 (1g/L silica, 10^{-6} M Th, I=1M $NaClO_4$)

(>6.5). While this assumption holds true for humic acid/ silica interaction, the same, may or may not be the case for silica/ EPS. Thus, treating the ternary system as a simple competition between the two ligands may not be a good one here. Furthermore, because we lack information on constants needed to describe a compositionally complex EPS in terms of its ability to simultaneously bind actinide ions and to the silica surface, it did not seem to noticeably shift the sorption curve, possibly due to the relatively strong surface activity of EPS. As seen in the study of the ternary system hematitie/natural organic matter

(NOM)/thorium (Murphy et al., 1999), potentiometric titrations on the components (silica and EPS) are needed to provide the necessary information on electrostatic and chemical terms for input into model programs such as FITEQL. Since this information was not acquired here, this was not attempted yet.

5.5 Conclusions

This study assesses the sorption of three actinides, thorium, protactinium and plutonium, on silica as a function of ionic strength and pH. As seen in several other studies, there appears to be no influence on the ionic strength of the solution indicating the formation of inner sphere complexes. A sorption edge of pH 2.5 to 4 was seen for both plutonium and thorium. A sorption edge for protactinium was not evident in the data. A series of non–complexing buffers, developed from the Good buffer series, were utilized here as a means of maintaining the target pH without perturbing the system with acid or base additions. This series of buffers appeared to work well in these experiments when compared to work of others that did not utilize buffers. Thorium showed the strongest association with the EPS followed by protactinium and then plutonium. Thorium and plutonium are expected to exhibit similar behavior as they are both tetravalent. In the binary system of silica/actinide, the log Kd for plutonium of 4.7 remained constant at pH >4.75. The log Kd for thorium on silica at near-neutral pH was slightly higher, i.e., 5, and also relatively constant above pH 4.75.

Lack of acquired thermodynamic data prevented strict modeling of this data, yet by comparing results to those of other studies, insights into the chemical processes that control surface sorption can be gained. The results from this study are comparable to those of Reiller et al. (2003), who investigated Th(IV) sorption to silica particles of 0.3 meq/g surface site concentrations over a pH range of 2 to 9, and those of Östhols (1995), who used 0.5 meq/g silica particles, with a surface area about 200 m^2/g for Th(IV) sorption experiments in the low pH <3. The specific surface area of silica particles that were used in this study, i.e., 500 m^2/g, were of similar magnitude. Thus, the conclusion by Reiller et al. (2003) that the binary system can be successfully modeled using SCM ignoring electrostatic terms would likely hold true for this data. Also, it is likely that their findings of significant solution complexes (thorium-humate) at pH >6 may also hold true for the EPS utilized here. In order to extend this study to be more directly comparable to literature model studies, it would be necessary to repeat the questionable (pH = 4 and 10) thorium data points, extend the pH range to lower pH values and conduct potentiometric titrations on both silica particles and EPS for data needed to input into a modeling program such as FITEQL.

6. SUMMARY

Several processes can influence the behavior of actinides in the environment but, in the case of particle-reactive actinides, sorption has a large control over their ultimate fate. Thorium, protactinium and plutonium are three particle-reactive actinides that have importance in different aquatic systems. Thorium and protactinium have been used as particle and colloid transport tracers for oceanic processes and plutonium has been found in several contaminated surface sites such as former nuclear weapons production facilities. Thorium is only found in the tetravalent (IV) oxidation state while protactinium and plutonium can occur in several oxidation states under typical environmental conditions. However, in most cases, the (IV) and (V) valence states are most prevalent and of most concern for Pu and Pa because of their contrasting behaviors. The (V) valence state is in general more soluble and hence more likely to be transported, while the (IV) valence state is more particle-reactive and thus, more likely to be sequestered. Thus, the overall objective of this study was to better understand the role of organic colloids in transport processes, such as surface sorption of actinide ions that can lead to mobilization or immobilization on particle surfaces in freshwater and marine systems. Sorption of metal ions to particles is often quantified by the particle-water partition coefficient (Kd), that is traditionally defined as the amount of the metal, i.e., actinide, associated with particles divided by the amount of the actinide remaining in solution. In addition to the traditional Kd, the Kd_c, which assumes a smaller size cutoff for what constitutes as particle, and thus combines

the colloids with the particles, while the dissolved fraction is the ultra-filter-passing fraction. The calculation of a Kd_c value allows for a comparison of colloidal associations with particles alone, i.e., the Kd value.

In order to accurately study processes controlling the fate of actinides in the environment, it is important that experimental conditions mimic the conditions found in the environment. A detailed look at the effects of varying experimental conditions on resulting sorption demonstrated the difficulty of studying these processes under environmental conditions. Working at extremely low, yet environmentally relevant, concentrations of actinides (10^{-12} to 10^{-15} M), causes difficulties in producing reproducible data given the presence of colloidal impurities which occur at orders of magnitude higher concentrations than the actinides under study. However, as was shown here, steps can be made to reduce these problems and better study the system. To date, most of the studies conducted, have failed to accomplish this because of the experimental difficulties one faces at low, i.e., fM concentrations and below. At best, experimental results were extrapolated from μM to mM concentrations, where only the weakest surface sites can be probed, thus ignoring the fact that surface sites on natural organic and inorganic colloids are heterogeneous. As a consequence, there is a distribution of sites of lower and lower abundance with higher and higher binding energy, thus leading to an inverse dependency of binding site concentrations and binding energy for most colloids. Thus, the first point that needed to be addressed was how to conduct a meaningful sorption experiment at environmentally relevant conditions, i.e., at near neutral pH, and

femto to picomolar concentrations of actinides. The purpose of this section therefore was to assess the effect of an organic colloidal third phase with minimal interference by colloidal impurities in solution. The optimization of experimental conditions under which to conduct environmentally relevant sorption studies included studies of seven different conditions: 1) method of particle separation, i.e., filtration or centrifugation; 2) the purity of the actinide tracer, i.e., trace metal or reagent grade acid; 3) type of container used for tracer storage, i.e., glass or Teflon; 4) pre-treatment of an acidic tracer in a near neutral solution, i.e., pre-neutralization or use of buffered solution; 5) ensuring a truly ionic tracer by pre-ultrafiltration; 6) pre-treatment of silica, i.e., pre-cleaned or not; 7) pre-treatment of the solution, i.e., clean-up columns and/or pre-ultrafiltration.

These seven conditions had varying effects on the extent of sorption, i.e., the Kd value. For the means of particle separation, filtration always resulted in a larger log Kd value. A consistently higher particle association in the case of filtration is believed to be the result of trapping of colloids on the filters. Therefore, when studying experimental conditions, the use of centrifugation was employed. However, when assessing particle-water partition coefficients from different studies in the literature, filtration is often carried out as that is the most common means of separation. The purity of the acid that was added, i.e., trace metal clean or reagent grade, had little effect on the sorption, but the type of storage container did. Thorium tracers stored in glass exhibited a lower log Kd value than those stored in Teflon. It is thought that this resulted from

association of the tracer with polysilicates leached from glass. The pre-treatment of silica and solutions had negligible effects on the resulting log Kd values. The experimental condition that had the greatest impact on the experimental results was how an acidic tracer was treated for use in experiments conducted at near neutral pH. Pre-neutralization with sodium hydroxide, the most common method of treating acidic tracers, resulted in a significant colloidal association to a non-surface reactive colloidal fraction, as compared to pre-neutralization with sodium bicarbonate, or use of buffered solutions. Where applicable, buffered solutions were thus used for particle-water interaction studies.

Plutonium and protactinium can occur in multiple oxidation states under different environmental conditions, with Pu occurring mostly as Pu(V) in organic matter poor environments such as groundwater, deep ocean water and rain water, and Pu occurring as Pu(IV) in organic matter rich environments, such as surface waters. Oxidation states (IV) and (V), however, have markedly different environmental behaviors. In order to study their respective behaviors, the efficacy of organic colloids, either commercially available, or extracted in the laboratory, as reductants of plutonium (V) to (IV) and as sorbing agents, rendering colloidal Pu more particle-reactive and thereby les mobile was tested. The reduction ability was tested by comparing the particle-water partition coefficients (Kd) of both oxidation states to silica particles with and without added organic molecule. In these experiments, it was assumed that increasing sorption with time of weakly sorbing Pu(V) could be attributed to Pu(V) reduction, i.e., the more weakly sorbing Pu(V) would first need to be reduced

before it could get more strongly sorbed. Thus, the resemblance of resulting Kd values to those of Pu(IV) indicate reduction of Pu(V). Results showed that the kinetics of Pu(V) sorption onto silica was relatively slow, and that it would take significantly more than 40 days to fully reduce Pu(V) to Pu(IV) using exopolymeric substances as organic reductants. A light/dark test for photoreduction on a 40-day time scale indicated that photoreduction does not cause any change in Pu(V) particle association. Of the commercially available organic compounds chosen to have the ability to reduce Pu(V) to Pu(IV) within 2 days, only hydroquinoe showed a significant increase in the log Kd value. Of the five bacteria and phytoplankton cultures studied for their reduction abilities, the EPS from *Psuedomonas fluorescens* Biovar II demonstrated the greatest ability to enhance log Kd of Pu(V), though the effect after 4 days was not large, likely due to slow kinetics. The study of reduction of Pu(V) to Pu(IV) by commercially available organic compounds (humic acid, hydroquinone, and glucose) as well as EPS extracted from several bacteria (*Pseudomonas fluorescens* Biovar II, *Sagittula stellata*) and phytoplankton *(Emiliani huxleyi, Synnecococcus*, and *Skeletonema costatum*) cultures did not show significant reduction on the short time scale but leaves open the possibility that given longer interaction times this could happen.

Thorium and Protactinium isotopes are important oceanographic tracers for paleo-ocean circulation, boundary scavenging, and sediment trap calibrations. In order to enhance our understanding of their tracer qualities and properties, particle-water partition coefficients were compared for these isotopes

using sediment trap particles from the Gulf of Mexico (GOM), as well as using archived sediment trap material from Bermuda Atlantic time series (BATS) and Hawaii oceanic time series (HOT) stations. Though these data sets were not directly comparable due to different preservation techniques, as well as depths of collection and therefore likely differing degrees of diagenetic alteration. Nonetheless, the sorption of thorium and protactinium isotopes to all three sediment trap sample sets resulted in some interesting observations. The GOM samples exhibited strong colloidal associations for all three isotopes. For the BATS samples, protactinium showed more of a colloidal association than thorium. The HOT samples showed no such colloidal association, likely as a result of formaldehyde (1%) and high salt (5%) concentrations that were used for sample preservation. These means of preservation could explain their tendency toward colloid flocculation and particle production, possibly accounting for higher particle associations and higher particle-water partitioning. One point of debate in the literature over recent years is the cause of fractionation of Th/Pa. Initially, the debate was which inorganic mineral phase would be causing preferential scavenging, and later, the effect of organics was evaluated. For the BATS samples, compositional information was correlated with the log Kd values. A significant and positive correlation was found between the log Kd value for thorium and the calcium carbonate content of the particles, as would be predicted from some earlier observations. However, extrapolation of the log Kd data to 100% calcium carbonate would yield a value that would be orders of magnitude higher than is observed in the laboratory. From these correlations,

one can infer that it is the co-occurrence of carbohydrate-rich organics with the calcium carbonate that is responsible for the enhanced scavenging of thorium. In fact, when EPS was added to silica or calcium carbonate, the ratio of thorium to protactinium or F(Th/Pa) increased from 14.16 to 25.2 for silica and 3.83 to 20.52 for calcium carbonate. Thus, the F(Th/PA) values for both silica and calcium carbonate in the presence of the EPS resulted in values similar in magnitude to those seen for the newly acquired (and "fresher") GOM samples, which showed values that were 10 times higher than the archived (and older) BATS and HOT samples.

In order to investigate competitive sorption by H^+, EPS and actinide ions, systematic study of plutonium, thorium and protactinium sorption onto silica particles with and without EPS as a function of ionic strength and pH was conducted. The treatment of an acidic tracer in near neutral pH had profound effects on experimental results was shown in Section 2, so a series of non-complexing buffers were utilized to study the pH range. As seen in previous studies, ionic strength does not significantly affect the extent of sorption indicating the formation of inner-sphere complexes. Modeling of the data as a function of pH was not attempted due to lack of necessary information on the silica particle and EPS surface properties. However, comparison of the data from this study to others under similar conditions shows a consistent trend over the range of investigated pH values. Thorium and plutonium exhibited typical cation behavior, with a sorption edge at a pH of 2.5-4. The sorption edge of protactinium was not observed, because no data below pH 4 were acquired.

These results contribute to a better understanding of the sorption of actinides onto particles, the main process that controls their fate in the environment. In groundwater, greater sorption leads to greater retardation, while in the ocean it leads to more efficient removal.

The impacts of the research findings will be as follows: Our understanding of the biogeochemical processes that control thorium and protactinium radionuclides that are used as oceanic tracers and of plutonium, which is present in a number of contaminated sites throughout this country is hampered by the presence of colloids in field and laboratory experiments. In the field, mobility and removal rates appear to be controlled by this colloidal phase, while in the laboratory, low levels of an uncharacterized colloidal phase are hampering experimental results at low levels of radionuclides. Controlled experiments studying the third phase, e.g., an organic colloid, in conjunction with actinides at low, environmental levels proved useful in identifying possible mechanisms of fractionating thorium and protactinium in the water column, and possible immobilization pathways of plutonium by EPS in terrestrial systems as part of a bioremediation strategy.

REFERENCES

Alhassanieh, O., Abdul-Hadi, A., Ghafar, M., Aba, A., 1999. Separation of Th, U, Pa, Ra and Ac from natural uranium and thorium series. Appl. Radiat. Isotopes 51, 493-498.

Allard, B., Kipatsi, H., Liljenzin, J.O., 1980. Expected species of uranium, neptunium and plutonium in neutral aqueous solutions. J. Inorg. Nucl. Chem. 42, 1015-1027.

Bacon, M.P., Cochran, J.K., Hirschberg, D., Hammar, T.R., Fleer, A.P., 1996. Export flux of carbon at the equator during the EqPac time-series cruises estimated from ^{234}Th measurements. Deep-Sea Res. 43, 1122-1154.

Bradbury, M.H. Baeyens, B., 2006. Modelling sorption data for the actinides Am(III, Np(V) and Pa(V) on montmorillonite. Radiochim. Acta 94, 619-625.

Bruno, J., 1990. The influence of dissolved carbon dioxide on trace metal speciation in seawater. Mar. Chem. 30, 231-240.

Buesseler, K.O., Bacon, M.P., Cochran, J.K., Livingston, H.D., 1992. Carbon and nitrogen export during the JGOFS North Atlantic Bloom Experiment estimated from ^{234}Th:^{238}U disequilibria. Deep-Sea Res. 39, 1115-1137.

Buffle, J., 1990. Complexation reactions in aquatic systems: An analytical approach. Ellis Horwood, New York.

Bundschuh, T., Knopp, R., Winzenbacher, R., Kim, J.I., Köster, R., 2001. Quantification of aquatic nano particles after different steps of Bodensee water purification with laser-induced breakdown detectin (LIBD). Acta Hydroch. Hydrob. 29, 7-15.

Chase, Z., Anderson, R.F., Fleisher, M.Q., Kubik, P.W., 2002. The influence of particle composition and particle flux on scavenging of Th, Pa and Be in the ocean. Earth Planet. Sc. Lett. 204, 215-229.

Chen, C., Wang, X., 2007. Sorption of Th(IV) to silica as a function of pH, humic/fulvic acid, ionic strength, electrolyte type. Appl. Radiat. Isotopes 65, 155-163.

Choppin, G.R., 2007. Actinide speciation in the environment. J. Radioanal. Nucl. Ch. 273(3), 695-703.

Choppin, G.R., 2003. Actinide speciation in the environment. Radiochim. Acta 91, 645-649.

Choppin, G.R., 1991. Redox speciation of plutonium in natural waters. J. Radioanal. Nucl. Chem. 147, 109-116.

Choppin, G.R., 1989. Humics and radionuclide migration. Radiochim. Acta 44/45, 23-28.

Choppin, G.R., 1983. Solution chemistry of actinides. Radiochim. Acta 32, 43-53.

Choppin, G.R., Morgenstern, A., 2001. Distribution and movement of environmental plutonium. In: Kudo, A., (Ed.), Plutonium in the Environment. Elsevier Science Ltd., New York, pp. 91-105.

Choppin, G.R., Nash, K.L., 1981. Dissociation kinetics of thorium and humic acid. J. Inorg. Nucl. Chem. 43, 357-359.

Choppin, G.R., Wong, P.J., 1998. The chemistry of actinide behavior in marine systems. Aquat. Geochem. 4, 77-101.

Choppin, G.R., Bond, A.H., Hromadka, P.M., 1997. Redox speciation of plutonium. J. Radioan. Nucl. Chem. 219(2), 203-210.

Cochran, J.K. 1992. The oceanic chemistry of the uranium and thorium series nuclides. In: Ivanovich, M. and Harmon, R.S. (Eds.) Uranium-series Disequilibrium: Application to Environmental Problems. Oxford University Press, Oxford. 2nd Edition. Pp. 334-395.

Dequeldre, C., Triay, I., Kim, J.I., Vilks, P., Laaksoharju, M., Miekeley, N., 2000. Groundwater colloid properties: A global approach. Appl. Geochem. 15, 1043-1051.

Doucet, F.J., Scneider, C., Bones, S.J., Kretchmer, A., Moss, I., Tekely, P., Exley, C., 2001. The formation of hydroxylamluminosilicates of geochemical and biological significance. Geochim. Cosmochim. Acta 65, 2461-2467.

Edwards, R.L., Chen, J.H., Ku, T.-L., Wasserburg, G.J., 1987. Precise timing of the last interglacial period from mass spectrometric determination of thorium-230 in corals. Science 236, 1547-1553.

Fanghänel, T., Neck, V., 2002. Aquatic chemistry and solubility phenomena of actinide oxides/hydroxides. Pure Appl. Chem. 72, 1895-1907.

Gaillard, J.F., Webb, S.M., Quintana, J.P.G., 2001. Quick x-ray absorption spectroscopy for determining metal speciation in environmental samples. J. Synchrot. Radiat. 8, 928-930.

Geibert, W., Usbeck, R., 2004. Adsorption of thorium and protactinium onto different particle types: Experimental findings. Geochim. Cosmochim. Acta 68(7), 1489-1501.

Good, N.E., Izawa, S., 1972. Hydrogen ion buffers. Methods Enzymol. 24, 53-68.

Greenwood, N.N., Earnshaw, A., 1998. Chemistry of the elements, 2nd ed., Butterworth Heinemann, Boston, MA.

Guo, L., Chen, M., Gueguen, C., 2002. Control of Pa/Th ratio by particulate chemical composition. Geophys. Res. Lett. 29(20), 1960.

Hirose, K., Tanoue, E., 2001. Strong ligands for thorim complexation in marine bacteria. Mar. Environ. Res. 51, 95-112.

Honeyman, B.D., 1991. Surface chemistry, colloids and trace element scavenging. In: Hurd, D. and Spencer, D., (Eds.) Marine Particles: Analysis and Characterization. Geophysical Monograph 63. American Geophysical Union, Washington, D.C. pp. 437-451.

Honeyman, B.D., Santschi, P.H., 1989. A Brownian-pumping model for trace metal scavenging: Evidence from Th isotopes, J. Mar. Res. 47(4), 951-992.

Hongxia, Z., Zheng, D., Zuyi, T., 2006. Sorption of thorium (IV) ions on gibbsite: Effects of contact time, pH, ionic strength, concentration, phosphate and fulvic acid. Colloid Surface A 278, 46-52.

Hoover, D.M., Drennan, C.L., Metzger, A.L., Osborne, C., Weber, C.H., Pattridge, K.A., Ludwig, M.L., 1999. Comparisons of wild-type and mutant flavodoxins from Anacystis nidulans. Structural determinants of the redox potentials. J. Mol. Biol. 294, 725-743.

Huh, C.A., Moore, W.S., Kadko, D.C., 1989. Oceanic ^{232}Th: a reconnaissance and implications of global distribution from maganese nodules. Geochim. Cosmochim. Acta 53, 1357-1366.

Hung, C.-C., Santschi, P.H., Gillow, J.B., 2005. Isolation and characterization of extracellular polysaccharides produced by *Pseudomonas fluorescens* BiovarII. Carbohyd. Polym. 61, 141-147.

Hunter, K.A., Hawke, D.J., Choo, L.K., 1988. Equilibrium adsorption of thorium by metal oxides in marine electrolytes. Geochim. Cosmochim. Acta 52, 627-636.

Iler, R.K., 1979. The chemistry of silica: Solubility polymerization, colloid and surface properties and biochemistry of silica. John Wiley and Sons, New York, NY.

Jakobsson, A.-M., 1999. Measurement and modeling of Th sorption onto TiO2. J. Colloid Interf. Sci. 220, 367-373.

Joshi, G.R., 1985. Lanthanum fluoride coprecipitation technique for the preparation of actinides for alpha-particle spectrometry. J. Radioanal. Nucl. Chem. 90(2), 409-414.

Kim, M.A., Panak, P.J., Yun, J.I., Kim, J.I., Klenze, R., Köhler, K., 2003. Interaction of actinides with aluminosilicate colloids in statu nascendi Part I: Generation and characterization of acitinide(III)-psueudocolloids. Colloid Surface A 216, 97-108.

Kumar, S., Tomar, B.S., Ramanathan, S., Manchanda, V.K., 2006. Effect of humic acid on cesium sorption on silica colloids. Radiochim. Acta 94, 369-373.

Langmuir D., Herman, J.S., 1980. The mobility of thorium in natural waters at low temperatures. Geochim. Cosmochim. Acta 44, 1753-1766.

Li, Y.-H., 2005. Controversy over the relationship between major components of sediment-trap materials and the bulk distribution coefficients of ^{230}Th, ^{231}Pa, and ^{10}Be. Earth Planet. Sci. Lett. 233, 1-7.

Luo, S., Ku, T.-L., 1999. Oceanic ^{231}Pa/^{230}Th ratio influenced by particle composition and remineralization. Earth Planet. Sci. Lett. 167, 183-195.

Luo, S., Ku, T.-L., 2004. On the importance of opal, carbonate and lithogenic clays in scavenging and fractionating Th-230, Pa-231, and Be-10 in the ocean. Earth Planet. Sci. Lett. 230, 201-211.

Martell, A.E., Smith, R.M., 1990. Critical stability constants. Plenum Press, New York.

Mayhew, S.G., 1999. The effects of pH and semiquinone formation on the oxidation-reduction potentials of flavin mononucleotide. Eur. J. Biochem. 265, 698-702.

Moran S.B., Weinstein, S.E., Edmonds, H.N., Smith, J.N., Kelly, R.P., Pilson, M.E.Q., Harrison, W.G., 2003. Does Th-234/U-238 disequilibrium provide an accurate record of the export flux of particulate organic carbon from the upper ocean? Limnol. Oceanogr. 48 (3): 1018-1029

Morse J.W., Choppin, G.R., 1986. Laboratory studies of plutonium in marine systems. Mar. Chem. 20, 73-89

Murphy, R.J., Lenhart, J.J., Honeyman, B.D., 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. Colloids Surface A 157, 47-62.

Nash, K.L., Choppin, G.R., 1980. Interaction of humic and fulvic acids with Th(IV). J. Inorg. Nuc. Chem. 42, 1045-1050.

Neck, V., Altmaier, M., Mueller, R., Bauer, A., Fanghanel, Th., Kim, J.I., 2003. Solubility of crystalline thorium dioxide. Radiochim. Acta 91, 253-262.

Niven, S.E.H., Moore, R.M., 1993. Thorium sorption in seawater suspensions of aluminum oxide particles. Geochim. Cosmochim. Acta 57(10), 2169-2179.

Östhols, E., 1995. Thorium sorption on amorphous silica. Geochim. Cosmochim. Acta 59, 1235-1249.

Pal'shin, E.S., Myasoedov, B.F., Davydov, A.V. 1970. Analytical chemistry of protactinium, Ann Arbor-Humphrey Science, Ann Arbor.

Panak, P.J., Kim, M.A., Yun, J.I., Kim, J.I., 2003. Interaction of actinides with aluminosilicate colloids in statu nascendi Part II: Spectroscopic speciation of colloid-borne actinides(III). Colloids SurfaceA 227, 93-103.

Quigley, M.S., Honeyman, B.D., Santschi, P.H., 1996. Thorium sorption in the marine environment: Equilibrium partitioning at the hematite/water interface, sorption/desorption kinetics and particle tracing. Aquat. Geochem. 1, 277-301.

Quigley, M.S., Santschi, P.H., Guo, L., Honeyman, B.D., 2001. Sorption irreversibility and coagulation behavior of ^{234}Th with marine organic matter. Mar. Chem. 76, 27-45.

Quigley, M.S., Santschi, P.H., Hung, C.-C., Guo, L., Honeyman, B.D., 2002. Importance of polysaccharides for ^{234}Th complexation to marine oranic matter. Limnol. and Oceanogr. 47, 367-377.

Reiller, P., Casanova, F., Moulin, V., 2005. Influence of addition order and contact time on thorium (IV) retention by hematite in the presence of humic acids. Env. Sci.Tech 39, 1641-1648.

Reiller, P., Moulin, V., Casanova, F., Dautel, C., 2003. On the study of Th(IV)-humic acid interactions by competition sorption studies with silica and determination of global interaction constants. Radiochim. Acta 91, 513-524.

Reiller, P., Moulin, V., Casanova, F., Dautel, C., 2002. Retention behaviour of humic substances onto surfaces and consequences upon thorium (IV) mobility: Case of iron oxides. Appl Geochem. 17, 1551-1562.

Runde, W., Conradson, S.D., Efurd, D.W., Lu, N.P., Van Pelt, C.E., Tait, C.D., 2002. Solubility and sorption of redox-sensitive radionuclides (Np, Pu) in J-13 water from the Yucca Mountain site: Comparison between experiment and theory. Appl. Geochem. 17(6), 837-853.

Runde, W., 2000. The chemical interaction of actinides in the environment. Los Alamos Science 26, 392-411.

Saito, T., Koopal, L.K., Nagasaki, S., Tanaka, S., 2005. Analysis of copper binding in the ternary system Cu2+/humic acid/ goethite at neutral to acidic pH. Environ. Sci. Technol. 39(13), 4886-4893.

Saito, A., Choppin, G.R., 1983. Separation of actinides in different oxidation states from neutral solutions by solvent extraction. Anal. Chem. 55, 2454-2457.

Saito, A., Roberts, R.A., Choppin, G.R., 1985. Preparation of solutions of tracer level Plutonium(V). Anal. Chem. 57, 390-391.

Sanchez, A.L., Murray, J.W., Sibley, T.H., 1985. The adsorption of plutonium IV and V on goethite. Geochim Cosmochim Ac 49, 2297-2307.

Santschi, P.H., Hung, C.-C., Guo, L., Pinckney, J., Schultz, G., Alvarado-Quiroz, N., Walsh, I., 2003. Control of acid polysaccharide production, and ^{234}Th and POC export fluxes by marine organisms, Geophys. Res. Lett. 30(2), 1044-1047.

Santschi, P.H., Roberts, K.A., Guo, L., 2002. Organic nature of colloidal actinides transported in surface water environments. Environ. Sci. Technol. 36, 3711-3719.

Santschi, P.H., Guo, L., Quigley, M.S., Baskaran, M., Walsh, I., 1999. Boundary exchange and scavenging of radionuclides in continental margin waters of the Middle Atlantic Bight: Implications for organic carbon fluxes. Cont. Shelf Res. 19, 609-636.

Santschi, P.H., Guo, L., Baskaran, M., Trumbore, S., Southon, J., Bianchi, T.S., Honeyman, B., Cifuentes, L., 1995. Isotopic evidence for the contemporary origin of high-molecular weight organic matter in oceanic environments, Geochim. Cosmochim. Acta 59(3), 625-631.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, John Wiley & Sons, New York.

Smith, R.M., Martell, A.D., 1989. Critical Stability Constants. Plenum Press, NY.

Verdugo, P., Alldredge, A.L., Azam, F., Kirchman, D.L., Passow, U., Santschi, P.H., 2004. The oceanic gel phase: A bridge in the DOM-POM continuum. Mar. Chem. 92, 67-85.

Walter, H.J., Geibert, W., Rutgers vad der Loeff, M.M., Fischer, G., and Bathmann, U. 2001. Shallow vs. deep-water scavenging of Pa-231 and Th-230 in radionuclide enriched waters of the Atlantic sector of the Southern Ocean. Deep-Sea Research I 48, 471-493.

Walther, C., 2003. Comparison of colloid investigations by single particle analytical techniques – a case study on thorium-oxyhydroxides. Colloid Surface A 217, 81-92.

Wang, X.K., Dong, W.M, Zhang, H.X., Tao, Z.Y., 2001. A multitracer study on the adorption of 36 elements on a silica: Effects of pH and fulvic acid. J. Radioanal. Nucl.Chem. 250(3), 491-496.

Weijuan, L., Zuyi, T., 2002. Comparative study on Th(IV) sorption on alumina and silica from aqueous solutions. J. Radioanal. Nucl. Chem. 254(1) 187-192.

Yu, Q., Kandegedara, A., Xu, Y., Rorabacher, D.B., 1997. Avoiding interferences from Good's buffers: A contiguous series of noncomplexing tertiary amine buffers covering the entire range of pH 3-11. Anal. Biochem. 253, 50-56.

Zeh, P., Kim, J.L., Marquardt, C.M., Artinger, R., 1999. The reduction of Np(V) in groundwater rich in humic substances. Radiochim. Acta 87, 23-28.

APPENDIX A. PRELIMINARY DATA USED FOR METHOD DEVELOPMENT FOR PARTICLE-WATER PARTITIONING EXPERIMENTS

Each data table varies one condition but the conditions from table to table vary. Therefore, it is only possible to view the tables individually for affect on the Log Kd value and not possible to compare between the tables.

Table A-1
Particle-water partitioning (Log Kd) value comparison between un-neutralized ^{234}Th tracer (pH~1) and ^{234}Th tracer pre-neutralized with NaOH (pH~7) with two different brands of silica (EM and PCR) and two different acid polysaccharides (Carageenan and xanthan)

ID	Si conc (g/L)	APS conc (mg/L)	Th pH ~1	Th pH =7
EM – Carageenan	5	0.5	1.5	4.6
EM – Xanthan	5	0.5	1.69	5.3
PCR – Carageenan	5	0.5	1.23	4.6
PCR - Xanthan	5	0.5	2.06	5.1

The above table shows log Kd values for the ternary system ^{234}Th, silica and Carageenan or gum xanthan. Experimental conditions were identical with the exception of the pH of the ^{234}Th tracer. In one case the ^{234}Th tracer is added in its acidic form directly to the $NaClO_4$ solution, identified as Th pH~1. In the other case the ^{234}Th is pre-neutralized with NaOH prior to addition to the batch system (Th pH~7). It is evident by these results that the acidic thorium tracer yields lower log Kd values (1.5 – 2) than when the Th tracer is pre-neutralized (4.6-5.3). There could be several reasons for the huge disparity between data. First, it could be a simple pH effect of the solution. By adding an extremely low pH tracer, the resulting solution pH could be lowered to the point of being below the sorption edge for Th resulting in low log Kd values. Alternatively,

the pre-neutralization of the tracer could result in species of thorium forming which are more strongly associated with particles resulting in higher log Kd values. Regardless of the reason for the difference, the difference is clear which indicates that some other experimental condition e.g. use of non-complexing buffers may be useful.

Table A-2
Comparison of Log Kd & Log Kc values for ^{234}Th under different batch solution pH values.

ID	Solution pH 2.5	Solution pH 8.2
Si	3.0	5.8
Si + Carageenan (I)	2.7	5.5
Carageenan (I)	4.2	5.1
Si + Xanthan	3.2	5.5
Xanthan	3.8	4.6
Si+Alginic	3.0	5.8
Alginic	4.2	5.3

The above data shows a direct comparison of the effect solution pH has on the log Kd values determined from binary (^{234}Th and acid polysaccharide) or ternary (^{234}Th, acid polysaccharide, and silica). There is clearly a pH effect on the log Kd values. A near neutral solution (pH = 8.2) producing log Kd values ranging from 4.6-5.8 while the solution pH = 2.5 for the same experiments produces log Kd values ranging from 2.7-4.2.

Table A-3
The effect of pre-ultrafiltration on the tris buffered experimental solution used for batch sorption experiments.

	Unclean	Clean
ASW Si	6.2	5.8
ASW Si+Carageenan (I)	6.8	-
ASW Carageenan (I)	5.9	5.2

- no measurable activity in the permeate fraction

The effect of pre-ultrafiltration is not clear from the data presented above. Due to the lack of clarity as well as the time consumption involved in pre-ultrafiltering, this pre-cleaning method will not be employed.

Table A-4
Comparison of the grade of acid (trace metal versus reagent grade) used for final dissolution of ^{234}Th production and the effect it has on log Kd values. Dirty (reagent acid) Th vs. Clean (TM grade) Th, both pre-neutralized with NaOH.

	Trace Metal grade acid (solution pH)	Reagent grade acid (solution pH)
Si	2.5 (7.3)	5.5 (8.3)
Si & Carageenan (I)	4.4 (8.5)	5.5 (8.3)
Carageenan (I)	3.5 (8.8)	5.1 (8.4)
Si & Xanthan	4.3 (8.7)	5.1 (8.3)
Si& Alginic Acid	4.4 (8.5)	5.6 (8.3)

While the procedure calls for use of trace metal grade acid for final dissolution in the procedure of milking ^{234}Th from ^{238}U, reagent grade was used on one occasion when trace metal grade was not available. During such time, it was noted that higher log Kd values where obtained and the effect was looked at more directly.

The above table demonstrates that at near neutral pH the type of reagent used for final dissolution of the ^{234}Th has an effect on the resulting log Kd values.

This is likely a result of higher amount of colloidal impurities in the reagent grade acid as it is stored in glass containers, which are more likely to produce aluminosilicate colloids that one would not expect from the trace metal grade acid as it is stored in Teflon.

Table A-5
Log Kd values comparing ^{234}Th Tracer neutralized with NaOH vs. NaHCO3, silica concentrations of 1 and 5 g/L and 0.1M and 1M NaClO4.

Conc NaClO4	Si conc.(g/L)	NaOH neut Th	NaHCO3 neut Th (pH ~ 8.2)
1M	5	5.35 (7)	3.48
	1		3.3
0.1M	5	4.35 (7.2)	3.74
	1		3.60

When NaOH is used to pre-neutralize the ^{234}Th tracer the log Kd values are always higher than when the tracer is neutralized with NaHCO3. The difference in silica concentrations (1mg/L vs. 5mg/L) was only tested with the NaHCO3 neutralized Th tracer, the higher concentration of silica has slightly higher log Kd values. Lastly, the ionic strength effect seems more pronounced in the sodium hydroxide neutralized Th tracer having much high log Kd in the higher ionic strength solution (1M) and in the sodium bicarbonate neutralized tracer the log Kd is only slightly higher in the lower ionic strength solution (0.1M)

Table A-6
^{234}Th log Kd values for pre-cleaned (1M NaOH and 1M HCl) versus unclean (straight from the bottle) silica particles.

Uncleaned Si (solution pH)	Cleaned Si (solution pH)
5.8 (8.2)	5.54 (8.3)

There is very little difference between the pre-cleaned and uncleaned silica particles. Since silica is pre-weighed into the centrifuge tubes for batch experiments, 1M HCl cleaning followed by triple rinse of deionized water and conditioning in the experimental solution will be carried out, as the tubes need to be cleaned prior to experimentation.

Table A-7
% of measured total ^{234}Th in each fraction to determine overall mass balance.

Fraction	ASW	ASW	ASW (pre – UF)	0.1M NaClO4 (column &pre-UF)
Retentate	20	13	19	64
Permeate	3	1	8	8
ultrafilter leach	22	12	15	7
Stir cell apparatus leach	-	-	29	10
Misc leach	6	5	38	12
Total	**51**	**32**	**109**	**101**

The above data demonstrate that in the untreated solution mass balances are much lower than for pre-treated in this case pre-ultrafiltered and clean – up columns and pre-ultrafiltered solutions. However, in the untreated solution experiments the stirred cell apparatus was not leached for loss which, as demonstrated by the pre-treated solutions, can be 10-30% of the total added

which would make these mass balances more reasonable. Yet, the pre-treatment does appear to produce better recoveries and pre-treatment therefore, the method of column cleanup using Chelex and XAD-8 will be utilized for this study. The data also strongly suggests that colloidal species of ^{234}Th strongly adsorb to the container walls, and that the leachability from container surfaces is affected by the relative surface-activity of the colloidal species.

Table A-8
Comparison of log Kd values for Pu and silica in the presence of EPS extracted from several different species.

	pH=2.1	pH=6.5	pH=8.1
Pseudomonas	5.0	5.7	
Clostridium	4.9	5.3	
Shewanella			5.9

There seems to be very little difference in the log Kd values between the EPS extracted from different species. The little difference that is seen between them may be explained by a pH effect as the log Kd values are slightly less in the lower pH solutions than those that are near neutral.

Table A-9
Comparison of log Kd values for Pu(IV) and Th in pre-ultrafiltered artificial seawater with 0.5g/L silica and 5mg/L Carageenan.

	Th (pH=7.6)		Pu (pH=8)	
	Part= Si	Part=Si+ret	Part= Si	Part=Si+ret
Si	5.3	5.8	4.4	4.5
Si+Carageenan (I)	5.3		3.9	3.9
Carageenan (I)	5.2		4.7	

Log Kd values for Pu are consistently lower than for those of Th under the same conditions. Though, Th and Pu are believed to have similar behaviors as the (IV) oxidation state is highly particle reactive, the difference may be indicative of other redox species of Pu in the solution, which would appear as a lower log Kd value. A more likely explanation is, however, is that the two tracers were not prepared with acids of the same purity. When trace metal grade acid was used to prepare the ^{234}Th tracer (Table AI-4), log Kd values of 4.4 for Si were determined, which is identical to that of Pu(IV), which was also prepared with trace metal grade acid.

APPENDIX B. SUPPLEMENTARY DATA FOR SECTION 3

Table B-1.
Colloid aggregation kinetics of pure Pu(IV) tracer. Size fractions of Pu(IV) tracer alone as a function of time where the % in each fraction is a percentage of the sum of the measured fractions and the mass balance is calculated based on the total Pu added.

Fraction	Time (day)	% sum of fractions		Mass balance
Particulate*	0.04	0.57	0.17	97 ± 6
Retentate	0.04	48.57	4.69	
Permeate	0.04	50.86	4.28	
Particulate[a]	1	1.08	0.21	86 ± 5
Retentate	1	33.01	2.80	
Permeate	1	65.91	4.15	
Particulate[a]	2	1.72	0.29	87 ± 5
Retentate	2	48.36	3.39	
Permeate	2	49.92	3.28	
Particulate[a]	5.95	17.62	1.66	47 ± 3
Retentate	5.95	46.27	5.36	
Permeate	5.95	36.11	3.18	
Particulate[a]	11.95	23.29	1.91	49 ± 2
Retentate	11.95	47.78	3.26	
Permeate	11.95	28.93	2.35	
Particulate[a]	17.94	33.96	1.48	58 ± 2
Retentate	17.94	35.33	1.62	
Permeate	17.94	30.71	1.39	
Particulate[a]	38.96	22.76	2.24	49 ± 3
Retentate	38.96	41.38	4.63	
Permeate	38.96	35.86	3.37	

[a]Sedimenting colloidal aggregates, collected by a 15 mL wash of the centrifuge tube after decanting into stirred cell.

Table B-2
Log Kd values (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc=fc/(fd*Cp) for Pu(IV) comparing humic acid, EPS from *Pseudomonas fluorescens* without protein removal (HP= 9.9% protein) and after protein removal (LP=4.7%)

Treatment	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total added)
Pu(IV)+Si	4.34	0.08	5.32	0.23			93
Pu(IV)+HA					5.91	0.35	22
Pu(IV)+Si+ HA	3.01	0.06	5.89[a]	0.5			92
Pu(IV)+Si	4.77	0.08	5.25	0.14			87
Pu(IV)+Pseud HP					5.74	0.05	80
Pu(IV)+Si+ Pseud HP	4.58	0.09	5.42	0.29			97
Pu(IV)+Pseud LP					6.6	0.14	88
Pu(IV)+Si+ Pseud LP	5.04	0.06	6.5*	0.4			100

[a]permeate value =0

Table B-3
Log Kd values (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc=fc/(fd*Cp) for Pu(IV) comparing humic acid, EPS from *Pseudomonas fluorescens* without protein removal (HP = 9.9% protein) and after protein removal (LP = 4.7%).

Treatment	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total added)
Pu(V)+Si	2.41	0.07	2.74	0.05			57
Pu(V)+HA					5.77	0.15	77
Pu(V)+Si+ HA	2.38	0.05	3.65	0.05			66
Pu(V)+Si	2.42	0.61	2.66	0.42			35
Pu(V)+Pseud HP					5.24	0.14	42
Pu(V)+Si+ Pseud HP	2.59	0.15	2.74	0.15			35
Pu(V)+Pseud LP					4.93	0.16	37
Pu(V)+Si+ Pseud LP	2.67	0.16	2.98	0.15			36

Table B-4
Log Kd values (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc=fc/(fd*Cp) for Pu(IV) with varying silica particle concentration.

Treatment	Cp (g/L)	Cc (g/L)	Log Kd	±	Log Kd_c	±	Mass Balance (% of total added)
Pu(IV)+Si	.005		5.06	0.003	6.14	0.004	68 ± 4
Pu(IV)+Si	.05		3.77	0.004	5.6	0.005	84 ± 5
Pu(IV)+Si	.5		4.88	0.006	5.56	0.013	101 ± 7
Pu(IV)+Si	5		4.39	0.013	4.82	0.019	107 ± 10
Pu(IV)+Si+Pseud	.005	.005	4.19	0.005	6.93	0.005	80 ± 5
Pu(IV)+Si+Pseud	.05	.005	4.24	0.006	5.92	0.006	90 ± 6
Pu(IV)+Si+Pseud	.5	.005	4.9	0.005	5.57	0.009	99 ± 6

Table B-5
Kd values for Pu(V) on silica in the presence of humic acid as a function of time. (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc=fc/(fd*Cp)

Treatment	Time (day)	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total)
Pu(V)+Si	2	2.83	0.04	2.91	0.04			82±4.3
Pu(V)+humic acid	2					5.66	0.05	84±4.9
Pu(V)+Si+ humic acid	2	2.50	0.04	3.59	0.04			76±3.7
Pu(V)+Si	7	3.04	0.03	3.15	0.03			93±4.3
Pu(V)+humic acid	7					5.70	0.05	86±5.0
Pu(V)+Si+ humic acid	7	2.77	0.04	3.7	0.04			86±4
Pu(V)+Si	21.1	3.2	0.04	3.34	0.04			81±4
Pu(V)+humic acid	21.1					5.45	0.05	78±4
Pu(V)+Si+ humic acid	21.1	1.53	0.09	3.91	0.05			127±8
Pu(V)+Si	34.01	3.33	0.04	3.48	0.04			89±4
Pu(V)+humic acid	34.01					6.17	0.05	71±4
Pu(V)+Si+ humic acid	34.01	3.22	0.04	4.35	0.05			78±4

Table B-6
Kd values for Pu(V) on silica in the presence of EPS extracted from *Pseudomonas fluorescens* as a function of time. (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc=fc/(fd*Cp)

Treatment	Time (day)	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total)
Pu(V)+Si	2.81	2.23	0.05	2.98	0.05			84
Pu(V)+Pseud	2.81					5.17	0.04	85
Pu(V)+Si+ Pseud	2.81	2.7	0.04	3.09	0.04			88
Pu(V)+Si	6.99	2.7	0.04	3.25	0.04			69
Pu(V)+Pseud	6.99					5.73	0.04	77
Pu(V)+Si+ Pseud	6.99	2.96	0.04	3.29	0.04			60
Pu(V)+Si	10.99	2.82	0.04	3.27	0.04			63
Pu(V)+Pseud	10.99					5.99	0.04	75
Pu(V)+Si+ Pseud	10.99	2.97	0.04	3.35	0.04			58
Pu(V)+Si	20.73	2.97	0.04	3.31	0.04			60
Pu(V)+Pseud	20.73					6.35	0.06	70
Pu(V)+Si+ Pseud	20.73	3.11	0.04	3.43	0.04			56
Pu(V)+Si	49.99	3.38	0.04	3.58	0.05			86
Pu(V)+Pseud	49.99					6.0	0.06	63
Pu(V)+Si+ Pseud	49.99	3.51	0.05	3.76	0.04			90

Table B-7.
Kd values for Pu(IV) on silica in the presence of EPS extracted from *Pseudomonas fluorescens* as a function of time. (Kd = fp/((fc+fd)*Cp), Kd_c = (fp+fc)/(fd*Cp), Kc=fc/(fd*Cp)

Treatment	Time (day)	Log Kd	±	Log Kd_c	±	Log Kc	±	Mass Balance (% of total)
Pu(IV)+Si	0.04	3.38	0.04	3.78	0.05			73.46±3.61
Pu(IV)+Pseud	0.04					6.26	0.06	65.04±4.2
Pu(IV)+Si+ Pseud	0.04	4.17	0.05	4.81	0.05			63.5±3.75
Pu(IV)+Si	1	4.66	0.06	5.01	0.06			71.4±4.71
Pu(IV)+Pseud	1					5.75	0.05	72.13±3.8
Pu(IV)+Si+ Pseud	1	4.77	5.04	5.04	.08			82.6±5.56
Pu(IV)+Si	2	4.49	0.05	4.93	0.07			71.17±4.38
Pu(IV)+Pseud	2					6.29	0.05	69.1±4.2
Pu(IV)+Si+ Pseud	2	4.47	.05	5.07	.07			77.2±4.5
Pu(IV)+Si	5.95	4.51	0.05	5.18	0.07			75.5±5.1
Pu(IV)+Pseud	5.95					6.46	0.07	61.8±4.6
Pu(IV)+Si+ Pseud	5.95	4.72	0.05	5.23	0.06			80.0±5.5
Pu(IV)+Si	11.9	4.57	0.05	5.12	0.08			77.7±4.8
Pu(IV)+Pseud	11.9					6.15	0.05	69.4±4.2
Pu(IV)+Si+ Pseud	11.9	5.12	0.08	5.18	0.09			68.9±4.4
Pu(IV)+Si	17.94	4.66	0.07	5.26	0.11			79.1±5.8
Pu(IV)+Pseud	17.94					6.32	0.03	71.0±3.7
Pu(IV)+Si+ Pseud	17.94	4.79	0.07	5.24	0.12			73.4±5.2
Pu(IV)+Si	38.96	4.61	0.06	5.23	0.13			63.6±4.3
Pu(IV)+Pseud	38.96					6.10	0.06	60.0±4.1
Pu(IV)+Si+ Pseud	38.96	4.85	0.06	5.35	0.11			68.5±4.3

Table B-8
Test for "lost" plutonium (IV) reported as % of total added.
% of total added in each fraction after a 2 day sorption of Pu(IV) and organic colloid followed by a 2 day resorption with organic colloid and silica particles to test if the "lost" Pu in the initial experiment is recoverable.

ID	Fraction	Sorption %	±	Resorption %	±
Pu(IV)+Pseudomonas	Particulate	-		3.8	0.5
	Retentate	8.64	0.9	1.63	0.4
	Permeate	3.79	0.7	0.23	0.1
	TOTAL	12.4	1.1	5.7	0.6
Pu(IV)+Humic Acid	Particulate	-		8.05	0.74
	Retentate	81.29	6.20	0.81	0.18
	Permeate	2.55	0.38	0.08	0.06
	TOTAL	83.6	6.2	8.9	0.8
Pu(IV)+Hydroquinone	Particulate	-		5.15	0.56
	Retentate	21.07	1.9	0.96	0.34
	Permeate	53.62	3.83	0.32	0.19
	TOTAL	74.7	6.4	6.4	0.7
Pu(IV)+glucose	Particulate	-		8.79	0.85
	Retentate	36.15	2.71	2.29	0.35
	Permeate	12.47	1.17	0.13	0.08
	TOTAL	48.6	3.0	11.2	0.9

Measured residual volume – insignificant.

Table B-9
Size fractions of Pu(V) tracer alone.

ID	Fraction	% of total added	+/-
Pu(V)-1	Particulate	3.3	0.3
	Retentate	6.2	0.9
	Permeate	41.8	3.0
Pu(V)-2	Particulate	3.9	0.6
	Retentate	6.8	1.1
	Permeate	37.6	3.2

Table B-10
Size fractions of Pu(V) tracer alone including diafiltration to test if tracer retained by the filter can be washed to the permeate.

ID	Fraction	% of total added	+/-	Mass Balance
Pu(V)-1	Retentate	2.21	0.48	82.4±6.3
	Permeate	66.44	6.13	
	Permeate 2	13.7	1.45	
Pu(V)-2	Retentate	3.22	0.62	85.9±5.2
	Permeate	67.8	4.94	
	Permeate 2	14.9	1.43	
Pu(V)-3	Retentate	5.2	0.5	80.5±4.8
	Permeate	64.8	4.7	
	Permeate2	9.7	0.8	
	Permeate3	0.5	0.1	
	Permeate 4	0.3	0.1	
Pu(V)-4	Retentate	3.5	0.4	89.9±5.3
	Permeate	71.5	5.2	
	Permeate2	13.9	1.1	
	Permeate3	0.7	0.1	
	Permeate 4	0.2	0.1	

Table B-11. Oxidation state determination run in duplicate of ^{240}Pu tracer using TTA extraction of (Saito and Choppin, 1983).

Replicate	Organic	Interface	Aqueous	% of total added
^{240}Pu -1	73.5 ± 4.1	5.08 ± 0.6	25.9 ± 5	104.4 ± 4.4
^{240}Pu -2	83.0 ± 4.6	20.2 ± 1.1	7.2 ± 0.5	110.4 ± 4.8

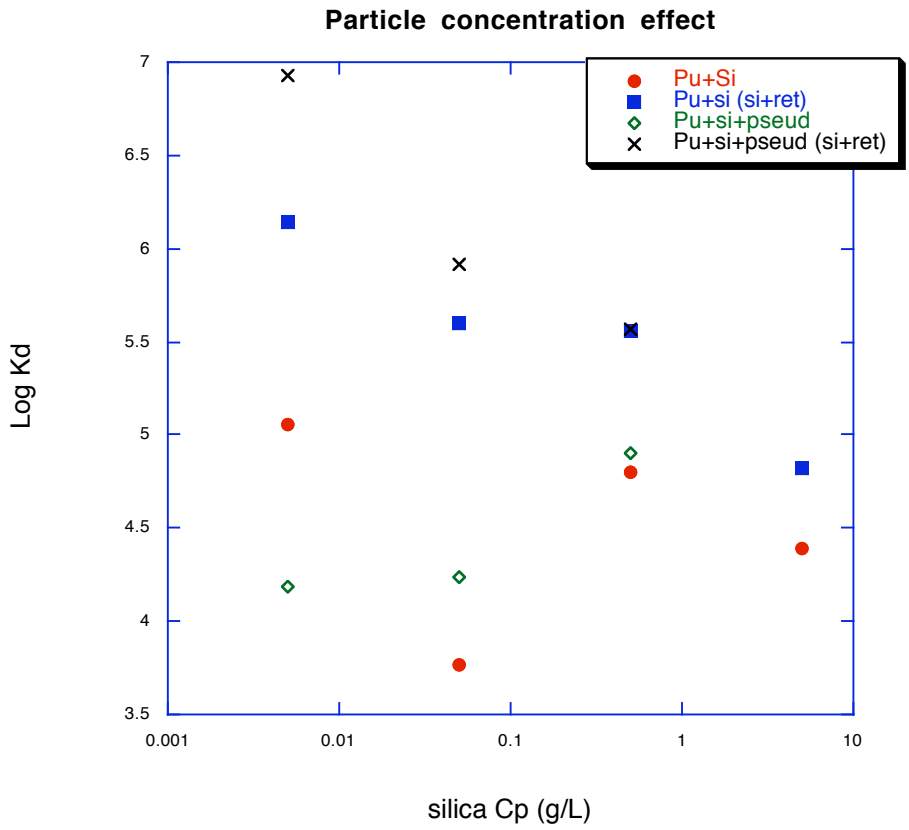

Figure B-1. Log Kd values for ternary system, plutonium, silica and *Pseudomonas fluoroscens* Biovar II in 0.1M $NaClO_4$ 50mM Tris/ 25mM HCl,

Lack of linearity possibly due to slight dissolution of silica, which would affect the lower concentrations of silica more so than the higher concentrations. Test was run for dissolution of silica and although up to 30% of silica may be dissolved over 2 days in the test solution, this does not significantly affect the resulting log Kd values.

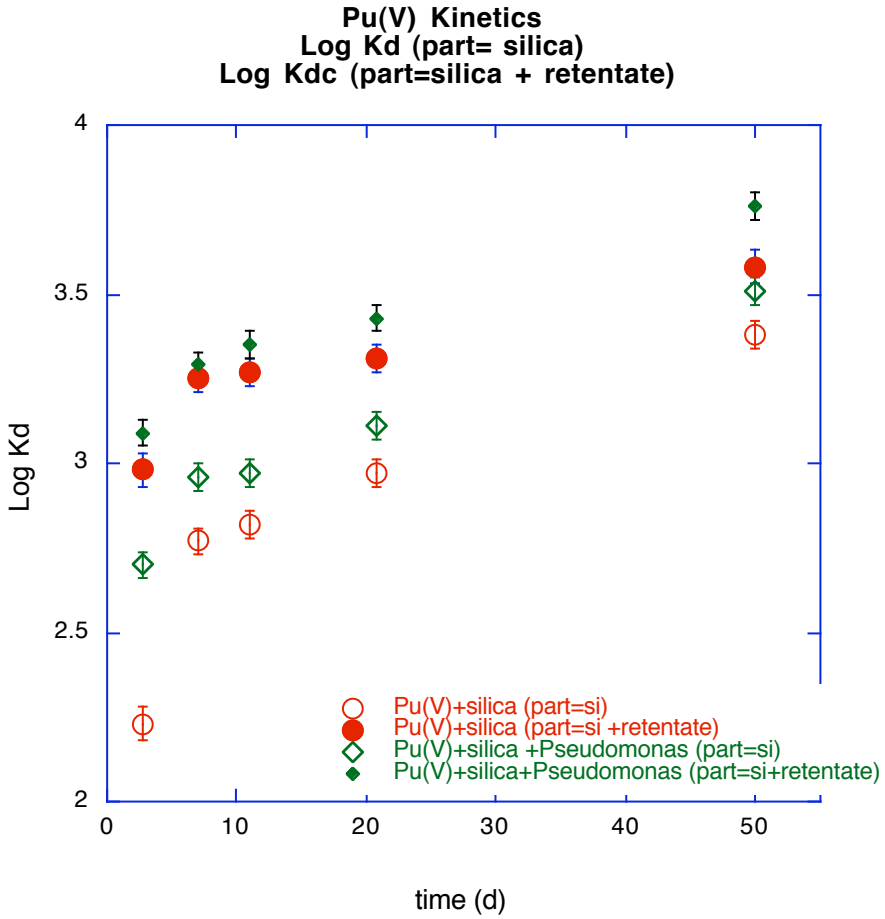

Figure B-2. Comparison of log Kd (open symbols) and log Kd_c (closed symbols) values for Pu(V), silica (0.5g/L) and *Pseudomonas fluroscens* Biovar II (5mg/L) in 0.1M $NaClO_4$ 50mM Tris/ 25mM HCl

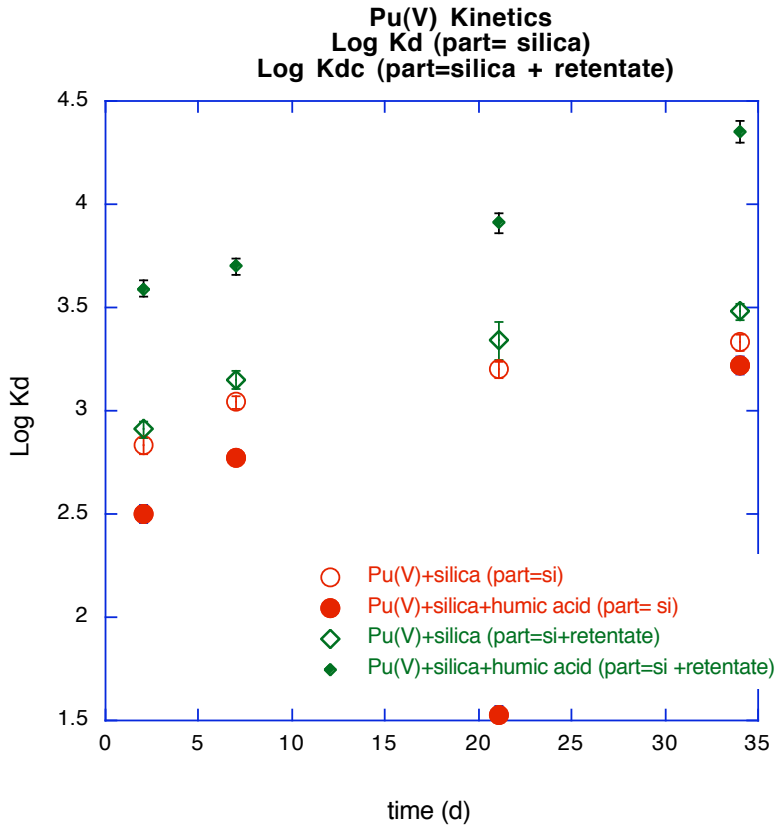

Figure B-3. Comparison of log Kd (open symbols) and log Kd_c (closed symbols) values for Pu(IV), silica and *Pseudomonas fluoroscens* Biovar II *i*n 0.1M NaClO4 50mMTris/ 25mM HCl, 0.5g/L silica and 5mg/L *Pseudomonas fluoroscens* Biovar II.

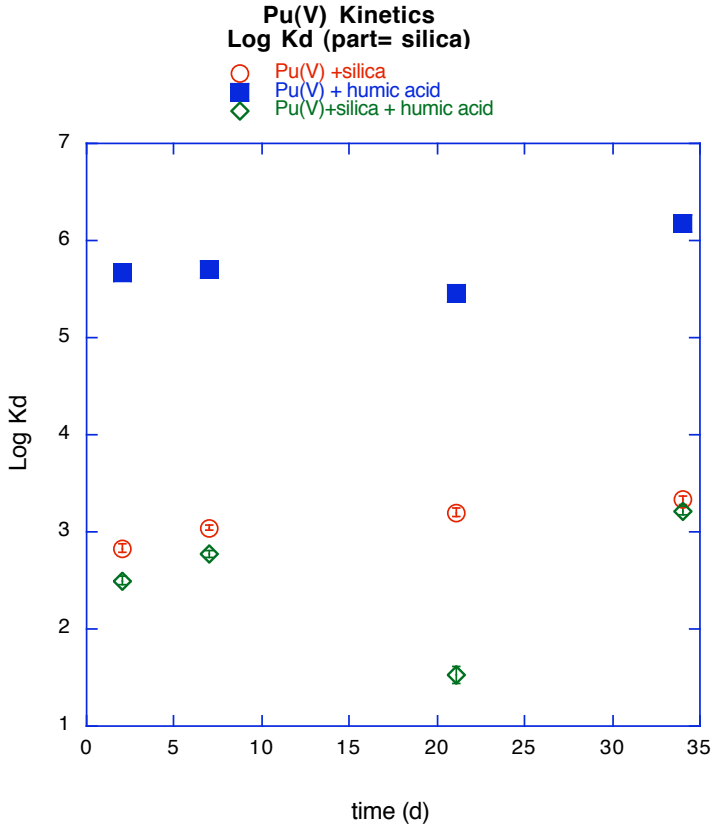

Figure B-4. Comparison of log Kd (open symbols) and log Kd_c (closed symbols) values for Pu(V), silica (0.5g/L) and humic acid (5mg/L) in 0.1M $NaClO_4$ 50mMTris/ 25mM HCl.

VITA

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